University of Alberta

Chiral PCBs in the Aquatic Food Web of Lac La Biche, Alberta, Canada

by

Joshua Morrissey ©

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Abstract

Concentrations and enantiomeric fractions of chiral polychlorinated biphenyl (PCB) congeners in Standard and Certified Reference Materials, and the biota of the Lac La Biche (LLB) aquatic food web were evaluated in order to ascertain the occurrence of PCB bioaccumulation and biotransformation. Bioaccumulation of PCB congeners was observed in biota of the LLB food web. In forage fish, there was little evidence of biotransformation of chiral PCBs. In predatory fish and piscivorous birds, extensive bioprocessing of PCB 95, 91, and 149 was observed, indicated by nonracemic enantiomeric fractions of these congeners. This may indicate the occurrence of cytochrome P-450 mediated biotransformation of these congeners. Bioaccumulation of both chiral and achiral PCB congeners was observed in fish of the LLB food web. Evidence of enantioselective maternal transfer of PCB congeners 95 and 149 from mother to egg was observed, as indicated by statistically different EFs observed in double-crested cormorants.

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Chapter 1: Introduction and Literature Review

Polychlorinated biphenyls (PCBs) are a class of organochlorine contaminant compounds that are ubiquitous in the environment. In this thesis, PCBs are measured in reference materials and biota of the Lac La Biche (LLB) aquatic food web. Chapter one introduces PCBs, their synthesis, and production. PCBs are compounds of environmental significance, due to their inherent toxicity and persistence in environmental compartments, which will be discussed in detail in sections 1.1.2.3 and 1.1.2.4, respectively.

Nineteen of the 209 possible PCB congeners have stable enantiomers. Section 1.2 defines chirality, and the properties of enantiomers. This includes differing enantioselective effects, potency, and toxicity. Enantiomers of chiral compounds may react differently to environmental processes. This is discussed in section 1.2.3. In order to determine whether or not this type of process is occurring, separation of enantiomers must occur in order to measure the enantiomeric fraction of the mixture. The means by which this is done is discussed in Section 1.3.

Once a persistent organic pollutant enters a food web, there are several significant processes that occur, which affect the overall fate of the pollutant. These processes include bioaccumulation, bioconcentration, biomagnification, and biotransformation. In order to determine the extent of these processes, two things must be known: the concentration of the pollutant in each food web constituent, and the trophic level of the organism consuming the pollutant. Section 1.4 outlines the means to measure trophic position, as well as discussing in detail the processes that are significant to the fate of a persistent organic pollutant in the environment.

In order to ensure that accurate enantiomer concentrations are being measured, reference material enantiomeric fractions (EFs) are measured. Reference materials are an integral component of quality assurance/quality control protocol. While the pollutant composition of many reference materials has been extensively quantified, there is little data on the enantiomer composition of such materials. In chapter 2, the enantiomer composition of additional Standard Reference Materials (SRMs) often used for organochlorine (OC) analytical method development and quality assurance/quality control are measured. A version of this chapter was previously published (Morrissey, Morrissey, J. A., Bleackley, D. S., Warner, N. A. and Wong, C. S., 2007. "Enantiomer fractions of polychlorinated biphenyls in three selected Standard Reference Materials." Chemosphere **66**(2): 326-331.) and is reproduced with permission (Copyright 2006, Elsevier Ltd.)

In the third chapter concentrations and enantiomeric fractions of chiral polychlorinated biphenyl (PCB) congeners in the biota of the Lac La Biche (LLB) aquatic food web are evaluated in order to ascertain the occurrence of PCB bioaccumulation and biotransformation. Enantioselective processes occurring in forage fish, predatory fish, and piscivorous bird tissues and eggs are discussed in detail in section 3.4.

Concluding remarks and recommendations for future research are offered in the fourth and final chapter.

1.1. Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) share a biphenyl backbone substituted with one to ten atoms of chlorine, consisting of the chemical formula $C_{12}Cl_XH_{10-X}$ (Figure 1). Several terms are used to distinguish similarities and differences of PCBs. PCB homologues have differing numbers of chlorine atoms (e.g., tetrachlorobiphenyl $n_{Cl} = 4$). PCB isomers differ in substitution pattern of the chlorine atoms about the biphenyl backbone (Figure 2). The chemical formula of each isomer is identical. Each group of PCB homologues has a specific number of isomers. PCB congener denotes each individual polychlorinated biphenyl compound. There are 209 possible polychlorinated biphenyls. A simplified nomenclature system has been introduced for polychlorinated biphenyls, often referred to as a convention of the International Union for Pure and Applied Chemistry (IUPAC), which assigns a number from 1 to 209 for each congener. Increasing chlorine substitution results in higher congener number. PCB congener substitution patterns may be found in Figure 2 (Frame, 1997). In addition to the IUPAC nomenclature rules for PCBs, Ballschmiter and Zell (BZ) (1980) proposed the BZ nomenclature system, which is identical to IUPAC conventions, with the exception of several congeners. The differences between these conventions lie in the assignment of the phenyl rings (e.g., 2,3',4'-Trichlorobiphenyl in IUPAC while it is 2',3,4-Trichlorobiphenyl in BZ). This is also true for PCBs 34, 76, 97, 98, 122, 123, 124, 125, 177, 196, and 199. Several modifications to the numbering system have been proposed, which are summarized in Mills et al. (2007).

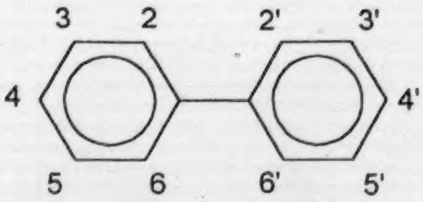

Figure 1: Biphenyl Backbone

1.1.1. Discovery and Use

Polychlorinated biphenyls were first synthesized in 1881 (Schmidt, 1881). Since then, their physical and chemical properties have made them ideal for use in industrial and electronic applications (Penning, 1930). PCBs were first mass-produced in the United States in 1929 (Alford-Stevens et al., 1985). The major trademark mixture of polychlorinated biphenyl is Aroclor, from Monsanto. Other trademark PCB mixtures include Askarel, Therminol, Kanechlor, and Clophen (Brinkman and de Kok, 1980). Production of polychlorinated biphenyls reached its peak in 1970, as about 37 million kg of Aroclor mixtures were produced in the United States (IARC, 1978). The manufacturing process for commercial PCB mixtures involves chlorination of biphenyl with anhydrous chlorine in the presence of a catalyst, usually iron or ferric chloride (Jenkins et al., 1930). The degree of chlorination of a mixture of PCBs is determined by the duration of reaction. Trademark names are usually followed by a number, which indicates total degree of chlorination of the mixture. Aroclor mixtures solely containing PCBs are classified by a four-digit number indicating the number of carbon atoms (12, indicating biphenyl) and the average percent chlorine of the mixture. For example, Aroclor 1268 contains greater percentages of higher chlorinated biphenyls than

Ring-Cl	2	3	4	23	24	25	26	34	35	234	235	236	245	246	345	2345	2346	2356	23456
23456																			209
2356																		202	208
2346																	197	201	207
2345																194	196	199	206
345															169	189	191	193	205
246														155	168	182	184	188	204
245													153	154	167	180	183	187	203
236												136	149	150	164	174	176	179	200
235											133	135	146	148	162	172	175	178	198
234										128	130	132	138	140	157	170	171	177	195
35									80	107	111	113	120	121	127	159	161	165	192
34								77	79	105	109	110	118	119	126	156	158	163	190
26							54	71	73	89	94	96	102	104	125	143	145	152	186
25						52	53	70	72	87	92	95	101	103	124	141	144	151	185
24					47	49	51	66	68	85	90	91	99	100	123	137	139	147	181
23				40	42	44	46	56	58	82	83	84	97	98	122	129	131	134	173
4			15	22	28	31	32	37	39	60	63	64	74	75	81	114	115	117	166
3		11	13	20	25	26	27	35	36	55	57	59	67	69	78	106	108	112	160
2	4	6	8	16	17	18	19	33	34	41	43	45	48	50	76	86	88	93	142
None	1	2	3	5	7	9	10	12	14	21	23	24	29	30	38	61	62	65	116

Figure 2: IUPAC PCB Congener Substitution Pattern Matrix (Frame, 1997a)

Aroclor 1242. A summary of some of the properties of Aroclor mixtures is given in Table 1. The exact congener pattern of PCBs in Aroclor mixtures varies somewhat by batch, due to the inexact and random nature of their synthesis (Frame et al., 1996).

Table 1: Comparison of Aroclor Mixtures (deVoogt and Brinkman, 1989)

Aroclor Mixture	Mean No. Cl/ Molecule	Approx. Wt.% Cl	Density (at 20°C)	Boiling Point Range (°C)
1221	1.15	21	1.18	275-320
1232	2	32	1.26	270-325
1242, 1016	3	40-42	1.37	323-366
1248	4	48	1.44	340-375
1254	5	54	1.54	365-390
1260	6	60	1.62	385-420
1262	6.8	62	1.64	390-425
1268	8.7	68	1.81	435-450
1270	10	71	1.95	450-460

1.1.2. Characteristics

1.1.2.1. Chemical and Physical Properties

Each PCB congener exhibits different physical and chemical properties such as water solubility, toxicity, melting point, vapor pressure, etc. Generally, increasing the chlorination of a PCB congener results in higher melting point, decreased water solubility, decreased vapour pressure, and increased chemical stability (Penning, 1930). Because of these properties, PCBs were applied for use as heat transfer fluids, dielectrics for transformers and capacitors, hydraulic fluids, plasticizers, adhesives, and inks (Moore and Ramamorthy, 1984). In addition to the physical differences between homologs, chlorine substitution plays a large factor in the properties of a PCB congener (Erickson, 2001). A summary of the properties of several PCB congeners is given in Table 2. The two-phenyl moieties can rotate freely about the single bond joining them. Because of this, low-energy conformations are obtained, based upon the steric hindrances of *ortho*-

chlorine atoms (Kaiser, 1974; Hansen, 1999). Non-*ortho* substituted PCB congeners can adopt a coplanar configuration, while *ortho*-substituted PCB congeners are rotationally stable, occupying different planes. PCBs of the latter type are termed atropisomers (Kaiser, 1974). Coplanar PCBs tend to exhibit biological activity and toxicity in a similar manner to of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). *Ortho*-substituted congeners have the capacity to exhibit chirality if the substitution is asymmetric between the phenyl rings. This will be discussed in greater detail in Section 1.2. Substitution patterns also affect photochemical degradation (Lepine and Milot, 1991) and shape-selectivity in chromatography (Sander and Parris, 1991).

Table 2: Properties of selected PCB congeners

IUPAC #	Substitution Pattern	Water Solubility (mg/L)	Henry's Law Constant (Pa m^3/mol)	Octanol/Water Partition Coefficient $\log k_{ow}$
49	24-25	0.090	17.38	6.1
77	34-34	0.017	9.52	6.1
95	236-25	0.021	20.06	6.4
136	236-236	0.006	22.99	6.5
138	234-245	0.001	10.84	6.7
153	245-245	0.001	13.37	8.1
180	2345-245	0.0003	3.24	7.2

1.1.2.2. Toxicology

1.1.2.2.1. Health Effects of PCB Exposure

PCBs have been linked to many different adverse effects throughout the body. Exposures to xenobiotics (chemicals not normally produced naturally by an organism) are classified into one of two categories: acute exposure, for single dosages, and chronic exposure, for repeated dosages over a period of greater than two months.

PCBs have a low acute toxicity. LD_{50} values in rats dosed with Aroclor mixtures range from 1250 mg/kg to 4000 mg/kg. In comparison, 2,3,7,8-TCDD, a very toxic compound, has an acute LD_{50} of 0.6 mg/kg. The mixture nature of PCBs makes assessing effects based on exposure a difficult task, as different congeners may have different toxicities and act in different manners. In addition, human exposure studies based on accidental exposures are confounded by possible interactions between PCB congeners, and other factors, such as previous PCB exposure from both the environment and diet, making it very difficult to determine the specific cause for the observed effects.

Chronic PCB exposure has been associated with a number of adverse health effects in various systems in humans such as hepatotoxicity, endocrine disorders, immunological alterations, skin conditions such as chloracne, neurodevelopmental changes, reduced birth weight, and cancer ((ATSDR), 2000).

Because PCBs are preferentially distributed to the liver, and have a long half-life in the body, hepatotoxicity is of concern. Studies of acute human exposure to PCBs have shown increased incidences of elevated microsomal enzyme concentration, and morphological evidence of liver damage (Kreiss et al., 1981; Kuratsune, 1989; Matsuda et al., 1984). The most common effects on the liver observed in PCB exposed laboratory animals are increases in relative liver weight and hepatic mixed-function oxidases, serum enzyme and cholesterol levels, nonneoplastic lesions, and/or tumors (Fish et al., 1997). Adverse effects such as fatty degeneration and hepatic necrosis have been observed in laboratory animals at chronic doses of Aroclor 1254 as low as 0.1-0.2 mg/kg/day (Fish et al., 1997).

Secondary health effects of PCBs at chronic dosages include induction of microsomal enzymes, which may lead to increased metabolic activity, and enhanced bioactivation of toxic substances (ATSDR 2000). Bioactivation refers to cases where a metabolite of a xenobiotic is significantly more toxic than its parent molecule. For example, the cytochrome P-450 (CYP) mediated biotransformation of benzo(*a*)pyrene can form an epoxide across the 4,5 carbon bone or the 7,8 carbon bond. The 7,8 epoxide is readily metabolized into a 7,8-diol, and further biotransformed into benzo(*a*)pyrene-7,8-dihydrodiol-9,10-epoxide by CYP-450. This molecule covalently binds DNA, and causes genetic mutations leading to lung and skin tumors (Keller and Jefcoate, 1984).

Suspicions that PCBs had adverse effects on the endocrine system, primarily the thyroid gland, arose when increased thyroid volume was reported in workers of a PCB production facility (Osius et al., 1999). Studies of experimental animals indicated that PCBs disrupt the production of thyroid hormones and interfere with their transport to receptors by binding to transthyretin, a thyroid hormone carrier (Brouwer et al., 1998). Changes in the physical structure of the thyroid gland have also been observed in rats (Kasza et al., 1978), perhaps suggesting that thyroid function is also altered.

Reduced serum levels of thyroid hormone T4 have been observed in rats exposed to both coplanar and non-coplanar PCBs (Morse et al., 1993). This reduction in hormone concentration is accounted for by the induction of UDP-glucuronosyltransferase (UDP-GT), an enzyme involved in Phase II metabolic processes. This enzyme facilitates the removal of thyroid hormone through metabolism in the liver (Hood and Klassen, 2000). The reduction in serum concentration of T4 induces production of thyroid stimulating hormone (TSH) via a negative feedback loop. As such, positive correlations between increased levels of TSH and PCB exposure have been observed in humans (Osius et al., 1999). The decreased serum levels in turn lead to hypothyroidism, a condition linked to premature birth, lower birth weight (Fein et al., 1984), behavioural deficiencies, developmental disorders, and lower IQ scores (Zoeller and Crofton, 2000).

PCBs have also been observed to affect other functions of the endocrine system, usually by disrupting steroid hormone signaling systems (Jonsson et al., 1975; Kuiper et al., 1998; Cooke et al., 2001). Mixtures of PCB congeners have been observed to produce estrogenic responses in laboratory animals (Hansen, 1998). Estrogenic responses have been observed for coplanar PCBs (Lind et al., 1999), noncoplanar PCBs (Geyer et al., 2000), and the hydroxylated metabolites of PCBs (Kester et al., 2000). A number of PCBs and hydroxylated metabolites of PCBs have also shown anti-estrogenic activity *in vitro* and *in vivo* (Moore et al., 1997; Geyer et al., 2000). PCBs have also been shown to affect the steroid production in other tissues such as the adrenal gland (Goldman and Yawetz, 1992), and in reproductive organs (Moore et al., 1985). There are a variety of mechanisms that PCBs act on the endocrine system, depending on the nature of the congener studied (Cooke et al., 2001). Mechanisms of endocrine disruption include alteration of hormone production, altering hormone metabolism, and acting as agonists for steroid receptors (Safe and Krishnan, 1995).

PCBs are currently listed as a suspected carcinogen by the International Agency for Research on Cancer (IARC) and the United States Environmental Protection Agency (USEPA). Increased cancer mortality in workers at PCB production plants indicates that PCBs are carcinogenic, particularly in the liver, biliary tract, intestines, and skin. Epidemiologic studies have indicated increased risk levels of pancreatic cancer and non-Hodgkin lymphoma (Hardell and Lindstrom, 1996), with increasing levels of PCBs, although in the studies conducted by Hardell and Lindstrom, the increased risk was not statistically significant.

Testing of carcinogenicity in rats indicates that PCBs are directly hepatocarcinogenic. PCB mixtures have produced negative results in mutagenicity tests, such as the Ames test (Heddle and Bruce, 1977). Mutagenicity was observed when PCB mixtures containing higher proportions of lower chlorinated PCBs were added to the Ames test in the presence of metabolic enzymes, suggesting that lower chlorinated PCBs can be bioactivated to produce mutagens (Wyndham et al., 1976).

PCBs for the most part are suspected to be indirect carcinogens. One pathway that PCB exposure may lead to cancer involves the induction of CYP and other enzymes involved in the metabolism of xenobiotics (Safe, 1994). The mechanism most frequently studied in the promotion of cancer is the induction of CYP as a result of the additive binding of PCBs to the aryl hydrocarbon (Ah) receptor, increasing the potential for carcinogenicity (Safe, 1994). This type of binding is similar to that of 2,3,7,8-TCDD, and is characteristic of dioxin-like compounds. In order to assess the degree of this type of toxicity, toxic equivalency factors (TEFs) are used to compare a toxicant's relative dioxin like toxicity to that of 2,3,7,8-TCDD. A list of the TEFs of the most toxic PCBs, normalized to that of 2,3,7,8-TCDD (TEF of 1) is listed in Table 3.

Table 3: Toxic equivalency factors for selected PCB congeners (Ahlborg et al., 1994).

IUPAC/BZ Congener Number	WHO TEFs (as of 1994)
77	0.0005
105	0.0001
114	0.0005
118	0.0001
123	0.0001
126	0.1
156	0.0005
157	0.0005
167	0.00001
169	0.01
170	0.0001
180	0.00001
189	0.0001

CYP enzymes produce reactive oxygen species, such as hydrogen peroxide and superoxide, as a by-product of xenobiotic metabolism leading to oxidative stress. Common events observed in the occurrence of oxidative stress include lipid peroxidation (Chow, 2000), oxidative DNA damage (Glauert et al., 2001), and changes in gene expression, all suspected to induce tumor production.

PCBs have also been observed to be neurotoxic. Neurodevelopmental alterations, such as hypoactive reflexes, slowed development of motor skills, and a greater likelihood of startling (Jacobson and Jacobson, 1984) have been observed in neonates and infants of women with a high PCB body burden. In rats, similar effects on motor activity are observed in adults after neonatal exposure (Schantz et al., 1997). PCBs also appear to affect higher brain function in rats, with significantly reduced maze performance after exposure to PCB congener mixtures (Schantz et al., 1995). The degree of neurotoxicity appears to be dependent on the number of chlorines in the *ortho*-position. Multi-*ortho* congeners appear to illicit stronger neurological effects than non- and mono-*ortho* congeners (Schantz et al., 1997).

Reproductive effects of PCB exposure are suspected in humans, based on experimental studies with rats and monkeys. Reduced conception rates, increased abortions, stillbirths, and decreased birth weight were observed in female rhesus monkeys exposed to chronic dosages of Aroclor 1248 and Aroclor 1254 as low as 0.02 mg/kg/day. (Arnold et al., 1993). Females are observed to be more sensitive to PCB exposure than males (Arnold et al., 1993). Studies of male monkeys indicate that PCB exposure may be associated with decreased sperm production and motility (Ahmad et al., 2003). PCB exposure has also been linked to decreasing sperm quality and testicular size in male mice (Fielden et al., 2001).

1.1.2.2.2. Toxicokinetics

There are four main components to be considered in the study of toxicokinetics of a substance: absorption, distribution, metabolism and elimination. These parameters are used to describe the path of a xenobiotic into, around, and out of an organism. They are congener-dependent, and are used to determine the body burden and exposure of an organism to xenobiotic compounds.

1.1.2.2.2.1. Absorption

1.1.2.2.2.1.1. Ingestion

Polychlorinated biphenyls can enter the human body by inhalation, ingestion, or dermal exposure. Of these portals of entry, ingestion is by far the most efficient and significant route of exposure for the general population. Absorption of PCBs occurs in the gut. Because PCBs are highly lipophilic, PCBs are absorbed by lymphatic circulation

(Hansen, 1999). This supports a passive diffusion model, where the concentration of the contaminant in blood is the major factor in absorption (Gobas, 2001). This absorption is also dependent on the fugacity gradient between two phases. Fugacity is a concept that was introduced by Lewis in 1901 as a means of more easily quantifying relative potentials of a chemical in various systems. The word fugacity is derived from Latin *fugere*, meaning "to flee" and is literally the potential of a molecule's tendency to exit a system. Molecules tend to move from environments of high fugacity to low fugacity. The fugacity of a substance is a physical property related to its ability, for example, to cross a membrane given current concentrations about the barrier. Based on fugacity potentials, the direction and extent of mass transfer can be predicted (Schwarzenbach et al., 2003).

The absorption of PCBs in by ingestion is very efficient. In a study of infant exposure to PCBs from breast milk, absorption was estimated as 96-98% efficient for a number of penta, hexa, and heptachlorobiphenyl congeners (McLachlan, 1993). These values were estimated using concentration differences between breast milk and infant feces. Similar results were observed by (Dahl et al., 1995), with absorption estimates of PCBs range from 90-100% for tetra- and higher noncoplanar polychlorinated biphenyls, and 60-98% for trichlorobiphenyls. The absorption of PCBs in the digestive system occurs rapidly. In mice, oral dosages of PCBs 52 and 77 produced increases in serum concentrations 4-7-fold within 1 hour of dosage. Maximum serum concentrations were reached approximately 2 hours after dosage (Darnerud et al., 1993; Yilmaz et al., 2006).

Further evidence of the high efficiency of PCB absorption was discovered by Schlummer et al. (1998), who conducted a mass balance to assess the absorption of polychlorinated biphenyls from food in humans of various ages (Schlummer et al., 1998).

Nearly complete absorption of coplanar PCB 126 was observed. This type of absorption is described by the fugacity of a contaminant, which will be discussed in greater detail in section 1.1.2.3.2.

In a study of background PCB exposure conducted by Duarte-Davidson and Jones (1994), the mean background exposure for an average person in the United Kingdom was estimated at 0.53 μg/person/day. Food consumption accounted for 97% of the total PCB exposure; air contributed 3.4% while water only contributed 0.04% (Duarte-Davidson et al., 1994). This is in agreement with the lipophilic character of PCBs. Congener patterns have also been shown to change depending on the type of food. Food containing higher lipidic material, such as meat, fish, and dairy contain significantly greater percentages of more highly chlorinated congeners. Freshwater fish account for 1.2% of the dietary exposure of PCB 28 and 27% of the dietary exposure to PCB 180 in the population studied. Conversely, vegetables account for 78% of the dietary exposure to PCB 28 and only 0.2% of the exposure to PCB 180 (Duarte-Davidson and Jones, 1994).

Similar absorption characteristics are observed in other vertebrates. Orally-dosed rats absorbed >90% of an administered dose of individual PCB congeners over a period of four days (Albro and Fishbein, 1972). This absorption was dose-independent, supporting the model for passive diffusion. Tanabe et al (1981) observed that absorption efficiency in rats decreased as the number of biphenyl chlorine atoms is increased. Dichlorobiphenyls and octachlorobiphenyls were absorbed with 95 and 75% efficiency, respectively (Tanabe et al., 1981). A model for the absorption of PCBs related to their octanol-water partition coefficient has been described in rainbow trout (*Oncorhynchus mykiss*) (Fisk et al., 1998). Absorption efficiency, $t_{1/2}$, and biomagnification factor

(BMF) have a curvilinear relationship with K_{ow}, with maxima observed at a log K_{ow} value of approximately 7. Decreasing BMFs at higher log K_{ow} values are attributed to slower kinetics of uptake and elimination, due to their larger size, as well as shorter exposure to superhydrophobic pollutants, due to lower bioavailability. This research suggests that K_{ow} may effectively be used to predict the environmental fate of hydrophobic pollutants (Fisk et al., 1998).

1.1.2.2.2.1.2. Inhalation

PCBs may also enter the body by inhalation. This can be a significant source of PCBs in occupational settings (WHO/IPCS, 1989). Occupational exposure to polychlorinated biphenyls may occur when working with PCB transformers, accidents, spills, or fires. Working with old appliances and electronics is also a significant source of household contamination (Borja et al. 2005). In this setting, the inhalation route may become a more significant route of exposure than ingestion. Wolff (1985) suggested that a maximum of 80% of the PCBs observed in adipose tissue of exposed capacitor-workers may have been absorbed by inhalation (Wolff, 1985). A similar correlation between blood serum and air concentrations has been reported in subjects involved in clean-up of a PCB transformer fire (Fitzgerald et al., 1986).

Because more highly chlorinated biphenyls are less volatile than less chlorinated polychlorinated biphenyls, exposure patterns to PCB mixtures also differ. In a study by Apfelbach et al. (1998), ferrets (*Mustela putorius furo*) were exposed to low levels of PCBs in ambient air over a period of 5 years. Polychlorinated biphenyls were observed in highest concentrations in olfactory tissue, with tetrachlorinated biphenyls as the major constituents. Congener profiles of adipose tissue in contaminated ferrets contained mainly hexa- and heptachlorinated biphenyls, indicating that selective retention of lower chlorinated PCBs takes place in the olfactory tissue in this exposure scenario (Apfelbach et al., 1998).

1.1.2.2.2.1.3. Dermal Exposure

Dermal exposure, like inhalation is a significant portal of entry in an occupational setting. Exposure to PCBs in this manner may also occur through skin contact with contaminated sediment and water for populations near the vicinity of hazardous waste sites (ATSDR, 2000). In studies using cadaver skin, up to 43% of Aroclor 1242 and 44% of Aroclor 1254 dosages prepared in water, mineral oil and soil were retained in the skin after 24 hours of contact (Wester et al., 1990; Wester et al., 1993). The congener profiles of the absorbed material were identical. The amount of dosage retained depends on the dosing vehicle, with water serving as the most efficient, followed by mineral oil and soil.

Dermal permeation rate constants were determined using single doses of radiolabelled mono-, di-, tri-, tetra-, and hexaclorobiphenyls were applied to the backs of rats (Garner and Matthews, 1998). An inverse relationship between penetration rate constant and degree of chlorination was observed (rate constants of 0.14, 0.074, 0.028, and 0.0058 hour^{-1} for mono-, di-, tri-, tetra-, and hexachlorobiphenyls, respectively) (Garner and Matthews, 1998). Exposure to PCBs in this manner may be reduced by washing the skin with soap and water following a known or suspected dermal exposure. After 15 minutes of exposure to Aroclor 1242, 93% of the applied dose was removed by washing with soap and water (Wester et al, 1990). The amount removed correlates inversely with time, as only 24% of an identical Aroclor dosage was removed after 24 hours of dermal exposure.

1.1.2.2.2.2. Distribution

Distribution refers to the destination of xenobiotics in the body after entry. Due to the highly lipophilic nature of PCBs, highest concentrations are found in adipose tissue once cleared from the bloodstream (ATSDR, 2000). PCB congener patterns in serum immediately after exposure reflect the congener profile of the contamination source. The availability of PCBs for distribution is linked to metabolism and excretion, which alter the PCB congener profile within 4-24 hours (Hansen, 1999). This observation suggests that tissue burden of PCBs must be based upon individual congeners or congener classes. One approach to assessing distribution involves the use of PCB 153 as a marker of total PCB concentration. PCB 153 is the most abundant and recalcitrant congener, and has been observed to have a high correlation with the total PCB concentration in human breast milk (r^2=0.99) (Johansen et al., 1994), and plasma (r^2=0.99) (Grimvall et al., 1997)

The tissue specific distribution of PCBs has been studied extensively in various organisms. In mice (Mizutani et al., 1977; Clevenger et al., 1989), preferential accumulation in adipose and liver tissue was observed, compared to accumulation in the thymus and kidney. Liver concentrations in monkeys were observed to be approximately double the concentrations in kidney and brain tissue (Allen et al., 1974). Chronic dose studies in rats indicate that highest PCB concentrations occur in adipose tissue, followed by liver and muscle tissue (Hashimoto et al., 1976). Intermediate concentrations were reported in skin, adrenal gland, and kidney tissue, preferentially distributed to the lipid fraction of each tissue.

1.1.2.2.2.3. Metabolism

Polychlorinated biphenyls, as previously mentioned are very lipophilic compounds, as demonstrated by their high octanol-water partition coefficients. As such, they are not readily removed from the body. In toxicology, the conversion of lipophilic xenobiotics to more hydrophilic xenobiotics to aid in excretion is termed metabolism. The more water-soluble compounds formed by metabolic processes are called metabolites, and vary depending on the metabolic pathway. In some cases, the metabolites of a toxicant may be more toxic than the toxicant itself. This is termed bioactivation. An overview of PCB metabolism is given in Figure 3 (Bandiera, 2003).

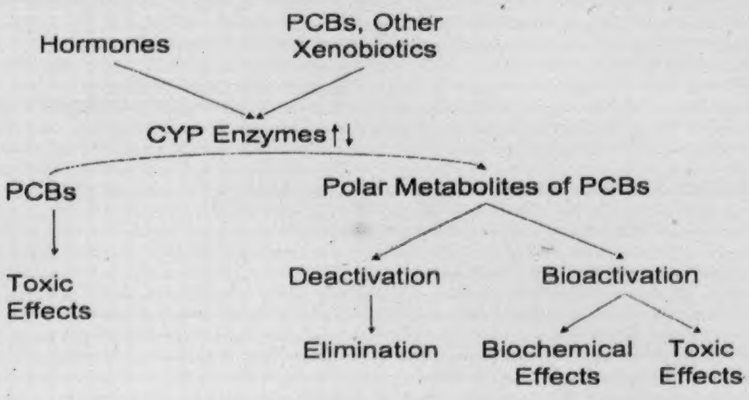
Hormones
PCBs, Other Xenobiotics
CYP Enzymes ↑↓
PCBs
Toxic Effects
Polar Metabolites of PCBs
Deactivation
Bioactivation
Elimination
Biochemical Effects
Toxic Effects

Figure 2: Cytochrome mediated metabolism

The metabolism of xenobiotics can occur in two phases, Phase I and Phase II. Phase I metabolism involves biotransformation of a xenobiotic into a more polar form, usually by the insertion of a more polar functional group to the xenobiotic. Phase II metabolism refers to bioprocesses occurring after Phase I metabolism, making the xenobiotic even more water-soluble to aid in excretion from the body.

The initial step in PCB biotransformation is regulated by the CYP enzymes (Matthews, 1982). CYP enzymes are a family of mixed-function oxidases, and serve many different functions in the body. CYP1A1, CYP1A2, CYP2B1 CYP2B2, and CYP3A enzymes mediate the addition of an oxygen atom to the PCB (Preston et al., 1984). As with previous toxicokinetic processes, the nature of this biotransformation and the metabolites formed are congener-specific. In general, more highly-chlorinated congeners are more resistant to biotransformation (Safe et al., 1980), and upon undergoing biotransformation, the metabolites may persist in the body.

The enzymes involved in PCB biotransformation vary with congener type, and may be divided into separate groups that are more amenable to CYP-mediated degradation. One category of PCBs chlorinated in the *meta* and *para* positions, but not in the *ortho*-positions, are effective inducers of CYP1A isozymes (Safe, 1994). Mono- and some di-*ortho*-substituted, non-planar PCBs induce isozymes from the CYP1A series, as well as some other classes, such as CYP2B (Brown, 1994). Di-*ortho*-substituted PCBs that are non-coplanar preferentially induce CYP2B enzymes, and induce CYP1A to a minor extent (Safe, 1994). PCB congeners that are non-coplanar and do not exhibit affinity to the Ah receptor primarily induce CYP3A enzymes, and CYP 2B enzymes to a minor extent. Hormones and other xenobiotics may also induce CYP metabolism. As illustrated above, there is also some overlap between classes of PCBs and the enzymes induced, as some mono-*ortho* PCBs may induce CYP1A and CYP2B enzymes (Safe et al., 1985). Because commercial PCB mixtures contain congeners from all of these groups, PCBs are best described as mixed-type inducers, as they may induce various CYP isoforms.

Depending on the substitution pattern, the mono-oxygenase reaction may occur in one of two ways. A hydroxylated-PCB (Figure 4) may be formed by direct insertion, preferentially in the *para*-position, unless sterically hindered by chlorine atoms in the *meta*-positions (Safe et al., 1980). An aromatic epoxide may also be formed (Figure 5) (Ishida et al., 1991). The expoxide is preferentially formed when hydrogen atoms inhabit adjacent positions on the phenyl ring. The aromatic epoxide may undergo rearrangement to form a hydroxylated PCB metabolite.

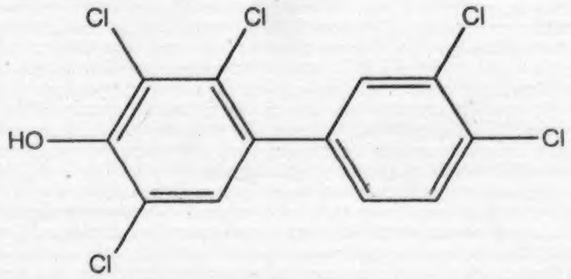

Figure 3: 4-Hydroxyl-2,3,3'4',5-pentachlorobiphenyl: A persistent metabolite

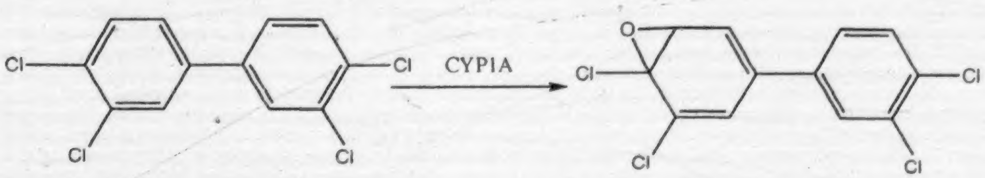

Figure 4: CYP1A-mediated formation of aromatic epoxide of PCB 77

Once the PCB is in its hydroxylated form, several processes may occur. The introduction of the hydroxyl group may increase water solubility to ease passage across biological membranes, and the molecule may be excreted from the body. Hydroxylated PCBs may also undergo further biotransformation in the liver to form glucuronide conjugates which are readily excreted in urine or feces (Schnellman et al., 1985). Highly chlorinated hydroxylated PCBs may also remain in the body for long periods of time. These metabolites themselves may exhibit toxicity by interacting with estrogen receptors and other enzymes of the endocrine system (Kester et al., 2000). Hydroxylated PCBs have also been reported to inhibit oxidative phosphorylation, and interact with transport proteins (Safe, 1994; Letcher et al., 2000).

Upon formation of the aromatic epoxide as described above, glutathione conjugation mediated by the enzyme glutathione-*s*-transferase may occur, leading to Phase II metabolism via the mercapturic acid pathway, forming methylsulfone metabolites (Figure 6) (Bakke et al., 1983; Preston et al., 1984). These metabolites are preferentially formed with the methylsulfonyl functional group at the 3- or 4-position of the biphenyl. As with hydroxylated PCBs, the methylsulfonyl metabolites may be excreted via urine or bile, or they may still remain lipophilic and stay in the body. In this case, tissue-specific retention of $MeSO_2$-PCBs has been observed in the cases of methylsulfonyl metabolites of PCBs 49, 87, 101, and 149, in which methylsulfonyl metabolites in the 3-position are preferentially retained in the liver, while 4-methylsulfonyl PCBs are preferentially retained in the adipose tissue (Letcher et al., 1995). Methylsulfonyl PCBs have also been observed to bind strongly to specific proteins such as uteroglobin (Gilner et al., 1988), and have been shown to induce several hepatic CYP enzymes and influence the endocrine system (Letcher et al., 2000). Methylsulfonyl metabolites of PCBs have also been shown to bioaccumulate through the food chain, and have been widely detected in the tissues of marine mammals (Bergman et al., 1994; Letcher and Norstrom, 1995) and humans (Noren et al., 1996).

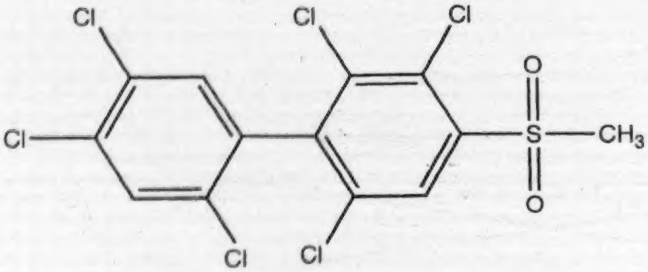

Figure 5: 4-Methylsulfonyl PCB 149

Because the enzymes involved in biotransformation of PCBs are chiral substrates, they may interact preferentially with single enantiomers of chiral PCBs. These interactions would alter the enantiomeric ratios of parent and metabolite molecules. Enantioselective biotransformation may be responsible for the nonracemic enantiomeric fractions observed in the freshwater invertebrate *Mysis relicta* (Warner and Wong, 2006), as well as at higher positions in the food web. This will be discussed in greater detail in section 1.2.4.2.

1.1.2.2.2.4. Excretion

PCBs are excreted from the body primarily through biliary excretion into the feces. Excretion into the urine is also a significant route of elimination (Allen et al., 1974). Because PCBs are lipophilic, significant amounts of PCBs are found in human milk, which can be eliminated via lactation. A woman may eliminate up to 10% of her body burden of PCBs in this manner (Abraham et al., 1994). This method represents a significant source of exposure to persistent organic pollutants in infants (Safe, 1984). This process has also been observed in other mammals such as mice (Sinjari et al., 1996), seals (*Callorhinus ursinus*) (Beckmen et al., 1999), and polar bears (*Ursus maritimus*)

(Bernhoft et al., 1997). Elimination of PCBs in avian species has been shown to occur in egg-laying, resulting in a significant decrease in body burden of PCBs in the mother bird. PCBs have also been observed in bird feathers (Dindal and Peterle, 1968).

As stated previously in this section, elimination of PCB congeners depends on the degree and position of chlorination. In studies of rats (Tanabe et al., 1981), di-, and trichlorobiphenyls exhibited elimination half-lives of 1-2 days, tetrachlorobiphenyls exhibited half-lives of 2-90 days, and hexachlorobiphenyls exhibited half-lives greater than 90 days. The half-life difference was attributed to a lower metabolic rate for the more highly chlorinated PCBs. In excretion studies in rats dosed with different configurations of polychlorinated biphenyl, PCBs with at least one pair of vicinal hydrogens were excreted much faster than other configurations, due to increased biotransformation rates (Gage and Holm, 1976). Excretion rates were greatly reduced by the presence of *ortho*-chlorines.

1.1.2.3. Occurrence in the environment

As early as the mid-1960s, chlorinated hydrocarbons were described as the most abundant synthetic pollutants in the global environment (Jensen, 1966). When PCBs were linked to decreasing egg thickness observed in birds in Great Britain and North America (Risebrough et al., 1968), the ubiquitous nature of PCB contamination (Risebrough et al., 1968; Epel and Lee, 1970; Holden, 1970; Richards et al., 1971; Tanabe, 1988; Lang, 1992; Muir et al., 1992) and negative effects observed (Ratcliff, 1967; Edwards, 1971; Fishbein, 1974) led to regulations on manufacturing, processing and distribution of PCBs by the USEPA. The Monsanto Chemical Company, producers of approximately 99% of industry-grade PCBs in North America, halted production of polychlorinated biphenyls in

1977 in accordance to the Toxic Substances Control Act (TCSA, 1977) regulations set by the United States government, a ban on PCB production in the United States was instituted, and regulations imposed on the use and disposal of materials containing polychlorinated biphenyls. Exemptions on the production of PCBs are limited to analytical and research usage (TCSA, 1977).

1.1.2.3.1. Atmospheric Occurrence

The atmosphere is a significant source of exposure to polychlorinated biphenyls. The atmosphere represents a major source of PCBs to aquatic ecosystems (Eisenreich and Strachan, 1992). PCBs enter the atmosphere by the process of volatilization (Simcik, 2001). Volatilization is directly related to temperature, as dictated by the Clausius-Clayperon equation (Equation 1):

$$\ln P = \left(\frac{\Delta H_V}{RT} \right) + const \qquad \textbf{Equation 1}$$

where P is the partial pressure of a compound, R is the molar gas constant (8.314 J mol^{-1} K^{-1}, ΔH_v is the enthalpy of vaporization, and T is the temperature in Kelvin. Because of this relationship between temperature and volatilization, atmospheric concentrations of persistent organic pollutants at the source of contamination are higher during warmer months, than during cooler winter months (Hillery et al., 1997; Cortes et al., 1998). In some cases, atmospheric concentrations are higher in the day than they are at night (Lee et al., 1998). This temperature dependence also brings about a consequence for colder ecosystems, such as the far north (Halsall, 2001), as PCBs undergo long-range atmospheric transport, which will be discussed in greater detail later in this section.

Air-water exchange is a significant process for the loading of PCBs to and from the atmosphere (Simcik, 2001). It represents a very important source of contamination of larger bodies of water, such as the Great Lakes by the atmosphere (Eisenreich and Strachan, 1992; Hillery et al., 1998). In order to assess the dynamics of air water exchange, it is useful to use the Henry's Law constant (HLC) of a chemical. The HLC, H, is defined as the partition coefficient between the partial pressure of the gas (P_{POP}) and dissolved phase of a compound ($C_{w,POP}$), and is calculated by Equation 2:

$$H = \frac{P_{POP}}{C_{w,POP}}$$ **Equation 2**

The HLC varies depending on the type of compound and the temperature. For example, there are differences in the HLC for different PCB congeners. However, since PCBs exhibit similar polarities, the differences in their HLCs vary only within an order of magnitude (Schwarzenbach et al., 2003).

Equation 2 is based upon a freshwater environment, but these results may be skewed depending on the contents of the water. For example, in a marine environment, the additional salt makes organic constituents less likely to be associated with the water. This is the "salting out" effect (Simcik, 2001). The increased ionic strength of the water affects the solubility of the organic molecules but has no effect on the gas phase. Henry's Law constant (H) increases because of this decreased affinity towards the dissolved phase. Conversely, increasing concentrations of organic materials have the opposite effect. The solubility of organic compounds is increased, and therefore H is decreased.

Once PCBs enter the atmosphere, several processes may occur. A substantial fraction of atmospheric PCBs exist in the gas phase, but because of the semivolatile nature of PCBs, partitioning onto (or into) airborne particulate matter (Simcik, 2001) is also a significant process. It must be noted that with increasing degree of chlorination of a PCB congener, increasing affinity to the airborne particulate phase is observed (Falconer and Bidleman, 1994). Depending on the composition of airborne particulate matter, two possibilities may be observed: the PCB congener may be absorbed into an organic-like matrix, or it may be adsorbed onto the surface of particulate matter. The distribution between the gas phase and the airborne particulate phase is described by its partition coefficient K_p (Equation 3):

$$K_p = \frac{\left(F/TSP\right)}{A}$$

Equation 3

In this equation, it is useful to normalise to the total suspended particulate matter, because the sorbate needs a substituent to which to sorb. K_p may be measured in the environment by measuring concentrations associated with filter-retained particulate matter (Particulate phase, denoted by F), and the adsorbent retained POP concentration (Gas phase, denoted by A).

The differences between the sampled concentrations in the above phases are negligible to the actual gas phase and particulate concentrations (Simcik, 2001). K_p affects the overall fate of a compound, as once the PCBs enter the atmosphere, the degree of association with the particulate phase affects the potential for atmospheric reactivity, deposition, and long-range atmospheric transport.

1.1.2.3.1.1. Atmospheric Processes Affecting PCBs

In the environment, photodegradation and biodegradation are the two main pathways for breakdown of PCBs (Erickson, 2001). The atmosphere is a reactive environment, because of the presence of oxidants such as •OH radical, O_3, and NO_3

(Anderson and Hites, 1996). Of the three oxidants, the •OH radical is the most significant for the removal of pollutants in the atmosphere. The •OH radical is formed from the photodissociation of ozone and subsequent reaction with water, as shown in Equations 4 and 5:

$$O_3 + h\upsilon \rightarrow O(^1D) + O_2 \qquad \textbf{Equation 4}$$

$$O(^1D) + H_2O \rightarrow 2(\bullet OH) \qquad \textbf{Equation 5}$$

where hυ represents a photon, and $O(^1D)$ represents an oxygen atom in an excited state. Anderson and Hites (1996) concluded that the major removal pathway for mono- to pentachlorobiphenyls in the atmosphere are photolysis reactions with the •OH radical, forming dechlorinated PCBs as well as chlorinated benzoic acids as products.

Photodegradation is more efficient for compounds in gas phase than for compounds portioned to atmospheric particulate matter. This is due to the particulate matter physically shielding the compound on its "dark" side (Behymer and Hites, 1985). Because of this, PCBs exhibit decreasing photodegradation rates with increasing degree of chlorination, because lower chlorinated biphenyls have a greater association with the gas phase (Simcik, 2001). Reducing the abundances of lower chlorinated biphenyls alters the initial congener PCB profile even further, skewing abundances towards more highly chlorinated PCBs, which exhibit greater affinities for airborne particulate matter, which protects them from •OH radical attack. Based on hydroxyl radical reaction rates, and known PCB reaction kinetics, atmospheric half-lives range from 3 days for trichlorobiphenyls to 500 days in the case of heptachlorobiphenyls (Sinkkonen and Passivierta, 2000). The efficiency of this process decreases with increasing chlorination, and in most cases does not significantly deplete PCB concentrations before ungergoing long range atmospheric transport

Another significant removal mechanism of PCBs in the atmosphere is via precipitation in the form of rain or snow, termed wet deposition. Several processes are important in the removal of PCBs in this manner. The processes involved in removal of atmospheric PCBs are illustrated in Figure 7 (Simcik, 2001). Partition processes occur between compounds in both gas and particulate phases, as well as within the raindrop itself. Atmospheric concentrations of POPs have been observed to decrease by 25-75% after a precipitation event.

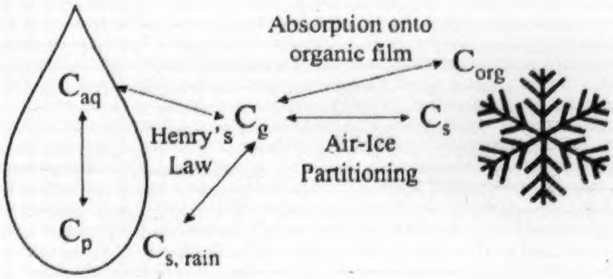

Figure 6: Exchange processes in rain and snow, adapted from Simcik (2001).

This process is termed washout, and may be calculated according to Equation 6:

$$W_T = \frac{C_{PRECIP}}{C_{ATM}}$$ **Equation 6**

where W_T is the total washout from the precipitation event, C_{PRECIP} and C_{ATM} are the concentrations of the pollutant in the precipitation and the atmosphere, respectively. Recall that PCBs are may be associated with a greater airborne particulate matter. Depending on the type of congener, it is washed out by different mechanisms.

In the gas phase, partitioning between the raindrop occurs. This is governed by Henry's Law constant for the pollutant as well as the temperature of the raindrop. If the droplet is small enough, the pollutant may partition to the air-water interface at the surface of the drop (Simcik et al., 1997). Pollutants associated with airborne particulate matter are removed from precipitation events by impaction, Brownian motion, and interception. The mechanism of particle washout is dependent on the size of the particle, which affects its inertia. In the case of snow, all of the above processes may occur, and there may also be organic material on the surface of the snowflake, and partitioning by adsorption mechanisms takes place. For particulate matter, the snowflake itself may function as a filter, allowing air to pass through the "pores" of the snowflake while large particles are trapped as it falls (Frantz and Eisenreich, 1998).

Dry deposition is another removal process of PCBs from the atmosphere. Dry deposition is a process involving both direct deposition from the gas phase (air-surface exchange) and particle deposition. The latter is the most significant to human exposure (Simcik, 2001). When gas-phase pollutants partition onto airborne particles, gas-phase exposure via inhalation is reduced, however the particle phase pollutants are delivered to areas where they enter food webs and may cause exposure by ingestion (Simcik, 2001). Dry deposition depends on the type and size of the particles, as well as the nature of the pollutant. The nature of the pollutant determines which phase to which the pollutant associates. Less volatile compounds will be strongly associated with the particulate phase than more volatile compounds.

Deposition velocities of particles vary with particle size. Larger particles with sufficient gravity have a greater deposition velocity, as do very small particles due to the effects of Brownian motion, or movement as a result of collisions from gas molecules (Simcik 2001). Particles with a diameter of 0.1 to 1 μm have a minimum deposition velocity, as they are too small to have appreciable mass and gravity, yet too large to be affected by gas molecules. Molecules of this size are significant sources of inhalation exposure, because particulate matter of this size may penetrate deep into the respiratory system, serving as a significant source of exposure to particle-bound pollutants.

1.1.2.3.1.2. Long Range Atmospheric Transport

PCBs and other persistent organic pollutants have been observed in the high Arctic since 1970, when they were observed in ringed seal (*Pusa hispida*) blubber (Holden, 1970). The primary source of this contamination was determined to be the atmosphere (Halsall, 2001). There are many transport mechanisms of PCBs, such as migrating birds, water currents, and air currents. The most important method in which persistent organic pollutants reach Arctic regions is via global fractionation or distillation (Wania and Mackay, 1996). This process has also been termed the "grasshopper effect".

Partitioning of PCBs occurs between the gas and particulate phases. Depending on the properties of the pollutant, this equilibrium may be more closely associated with one phase or another, as dictated by its vapour pressure, and the ambient temperature (Wania and Mackay, 1996). The process of evaporation and deposition operated in a continuous cycle with fluctuations in temperature, such as day and night temperatures, and summer and winter temperatures. Warmer temperatures favour evaporation, while cooler temperatures favour condensation, and deposition onto surfaces

Prevailing wind currents on the Earth, in general, move in a direction from the tropics to the polar regions (Borchert, 1953). Based on this, pollutants initially located in tropical regions evaporate efficiently, because of warmer temperatures. These pollutants migrate towards higher latitudes where cooler temperatures cause condensation of POPs. An increase in temperature in the summer results in further evaporation and migration until cooler temperatures are encountered. This cycle continues until ambient temperatures are too low for subsequent evaporation of the POP. The net result is a process where evaporation rates exceed deposition rates in the tropics, and deposition greatly exceeds evaporation in polar regions (Wania and Mackay, 1996). The degree of this latitudinal fraction is dependent on the nature of the contaminant, as more volatile chemicals tend to remain airborne for longer, and migrate faster and farther, whereas less volatile compounds will reside on surfaces longer and be more relevant to lower latitudes (Wania and Mackay, 1996).

In studies of the Canadian Arctic (Stern et al., 1997) and Europe (Ockenden et al., 1998) air concentrations of PCBs exhibited this type or fractionation. A latitudinal change in relative and absolute concentrations of PCB homolog groups was observed. More highly chlorinated biphenyls were observed in greater predominance at lower latitudes, and were found to be less transportable than lower chlorinated PCB congeners which were present in greater abundance at higher latitudes. Moderately chlorinated PCB congeners were evenly distributed, with similar concentrations reported throughout the sampling range (Ockenden et al., 1998). In studies of lake sediment (Muir et al., 1996), the proportion of di- and tri-chlorobiphenyls increased with latitude, while the octachlorinated PCBs decreased significantly. This process is analogous to chromatography, with the Earth's surface serving as the stationary phase, and the atmosphere the mobile phase (Halsall, 2001). Like chromatography, partitioning is responsible for the overall mobility of an analyte.

The process of long-range atmospheric transport to extremely high latitudes is a slow process, taking a period of years to decades. In the previous study of lake sediment by Muir et al. (1996), dated core samples indicate the onset of PCB contamination occurred in the 1950s and 1960s in the high Arctic. This is in comparison to the deposition onset at mid-latitudes and the sub-Arctic, which occurred in the 1920s and 1930s (Muir et al., 1996). Not all pollutants reach polar regions. Many are photodegraded en route, or are deposited into a sink (e.g., deep ocean sediments) and retained for long periods of time (Erickson, 2001).

1.1.2.3.2. Aquatic Behaviour and Fate of PCBs

Once deposited into the aquatic environment, several partitioning processes occur that are unique. There are several different phases in this type of system, the water, waterborne particulate, sediment, and biota. Similar to the atmosphere, PCBs are either dissolved into or adsorbed onto particles in the water column (Eisenreich, 1987). The presence of organic material in the water column leads to larger than expected water concentrations of PCBs. Dissolved organic material (DOM), such as humic material may greatly enhance the apparent solubility of PCBs, despite PCBs not being hydrophilic compounds.

PCB loss from the water mass occurs by partitioning into the air via air-water exchange, partitioning into the sediment compartment, and by sedimentation of waterborne particulate matter with PCBs sorbed to it (Eisenreich, 1987). In the case of Lake Superior, volatilization is the primary loss process, occurring by a factor of 17 times faster than sedimentation (Jeremiason et al., 1994). The sediment is complex, as it may be thought of as both a sink for PCBs as well as a source of PCBs to the water column. Once in the sediment, several processes are responsible for release into the water column including resuspension of particulate matter, and desorption to the water (Eisenreich, 1987). These processes occur simultaneously, and their direction is determined by their fugacity gradient (Mackay, 1979).

1.1.2.3.3. Processes Occurring in Sediment

Sediment was initially thought of as the major worldwide sink for PCBs, storing PCBs and other POPs for very long periods of time (NRC, 1979) until they are degraded by microorganisms. However, as concentrations of PCBs in water are on the decline (Jeremiason et al., 1998), the sediment may become a source for major PCB contamination to the water above. As dissolved PCBs are removed by volatilization, the partition equilibrium shifts to favour transfer of PCBs from the sediment to the water. A major pathway for the elimination of PCBs from the sediment is biodegradation. Biodegradation refers to the reactions of contaminants mediated by microbes. Anaerobic degradation is important in the aquatic environment, sediment, and soil. This serves as a useful environmental endpoint for PCB contaminanted sites (Bedard and Quensen, 1995). This process is generally very slow, with elimination half-lives on the order of years to decades.

Microbial biodegradation can occur through two mechanisms. Under aerobic or oxidizing conditions, microorganisms preferentially hydroxylate less chlorinated congeners, ultimately breaking open the phenyl rings to produce carbon dioxide, water and chloride ions through a chlorinated benzoic acid intermediate, effectively destroying the PCB (Furukawa et al., 1979). Anaerobic microbial degradation is also a pathway of significance to sediment-bound PCBs. The main process that occurs under these reducing conditions is reductive dechlorination (Bedard, 2001). Microorganisms partially dechlorinate highly chlorinated PCBs forming less chlorinated PCB congeners.

Microbial dechlorination is a very important process in dictating the fate and effects of PCBs in the environment. Microbial dechlorination of PCBs reduces the "dioxin-like" toxicity because it targets *meta* and *para* chlorines (Quensen et al., 1988; Bedard and Quensen, 1995). Dechlorination of *ortho* chlorines is sterically hindered by the close proximity to the phenyl ring. However, *ortho*-substituted congeners are significantly less toxic via the AhR pathway. Dechlorination also significantly reduces bioaccumulation and persistence of highly chlorinated PCB congeners by converting them to congeners with much shorter half-lives (Bedard and May, 1996), and making metabolism more favorable by reducing the number of chlorines which can sterically hinder metabolism by mixed function oxidases (James, 2001).

This process was first observed in 1984 in a study of PCBs in the Hudson River (Brown et al., 1984). Significantly different congener profiles were observed in sediment when compared to congener profiles of the original Aroclor composition. A higher proportion of mono- and dichlorobiphenyls and depletion of higher chlorinated biphenyls was observed. This observation was later confirmed under laboratory conditions (Quensen et al., 1988), who used microorganisms from Hudson River sediment in microcosm spiked with Aroclor. Anaerobic dechlorination of PCBs has since been reported worldwide (Bedard and May, 1996; Quensen and Tiedje, 1997; Cho et al., 2002; Magar et al., 2005).

Several mechanisms of dechlorination have been derived from laboratory microcosm studies. These processes are outlined in Table 4 (Bedard and Quensen, 1995). These processes may be expressed by unique populations of microbes, or a single population may express more than one type of dechlorination activity. For example, the microbial community of the Hudson River has been observed to dechlorinate PCBs via processes H, M and Q (Quensen et al., 1998). This process is illustrated in Figure 8. It is thought that the process of microbial reductive dechlorination is a cometabolic process (Fortin et al., 2006), meaning that the microbes involved do not actively metabolize the PCBs, rather they metabolize the PCBs because they are already metabolizing other substrates. This is suggested by the observation that PCB dechlorination that occurs in a laboratory setting may not occur *in situ* (Quensen and Tiedje, 1997). Dechlorination has also been observed to be "primed" by the addition of other substrates to the sediment (Bedard et al., 1993). In that study, it was observed that the addition of 2,6-dibromobiphenyl increased dechlorination rates by a factor of 1000. Such increases may allow for faster PCB remediation in contaminated sediments, if done in an environmentally feasible and cost-effective manner (Bedard, 2001).

Table 4: Microbial dechlorination activities. Targeted chlorine(s) are underlined (Bedard, 2001)

Process	Targeted Chlorine	Homolog Range	Reactive Chlorophenyl Groups
P	Flanked *para*	4-6	$3\underline{4}$, $23\underline{4}$, $2\underline{4}5$, $23\underline{4}5$, $23\underline{4}56$
H	Flanked *para*	4-7	$3\underline{4}$, $2\underline{3}4^{a}$, $2\underline{4}5$, $23\underline{4}5$
H'	Flanked *para*	3-5	$2\underline{3}^{a}$, $3\underline{4}$, $2\underline{3}4^{a}$, $2\underline{4}5$, $23\underline{4}5$
N	Flanked *meta*	5-9	$2\underline{3}4$, $2\underline{3}6$, $24\underline{5}$, $2\underline{3}4\underline{5}$, $2\underline{3}46$, $2\underline{3}4\underline{5}6$
M	Flanked & unflanked *meta*	2-4	$\underline{3}$, $2\underline{3}$, $2\underline{5}$, $\underline{3}4$, $2\underline{3}4$, $2\underline{3}6$
Q	Flanked & unflanked *para*	2-4	$\underline{4}$, $2\underline{3}^{a}$, $2\underline{4}$, $3\underline{4}$, $2\underline{3}4^{a}$, $2\underline{4}5$, $2\underline{4}6$
LP	Flanked & unflanked *para*	3-6	$2\underline{4}$, $2\underline{4}6$
T	Doubly flanked *meta*	7-8	$2\underline{3}45$

[a] *meta* chlorines are also targeted by this process

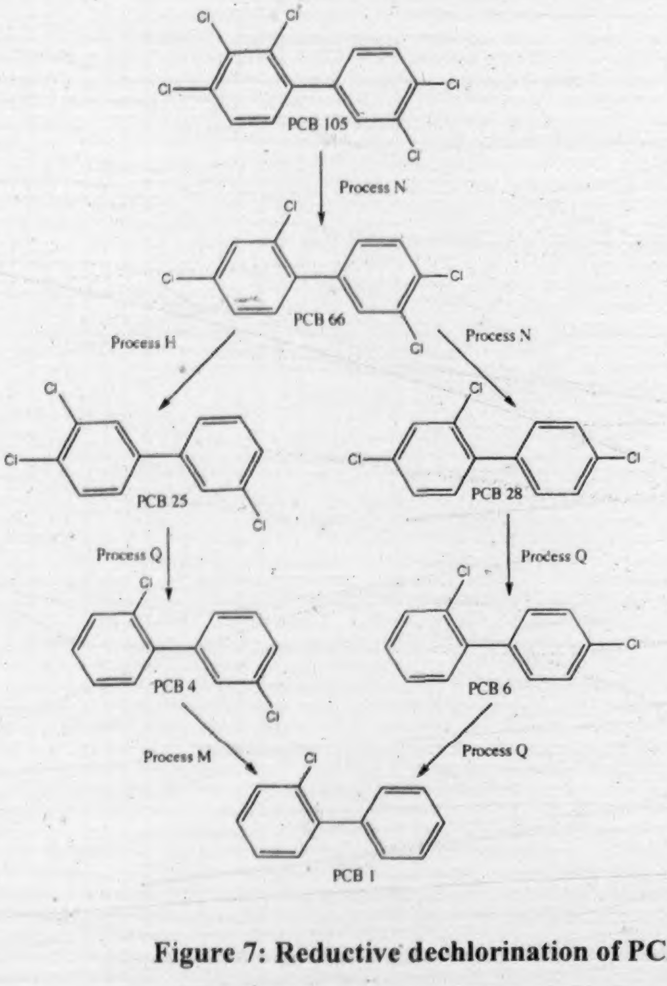
Cl
Cl
Cl
Cl
Cl
PCB 105
Process N
Cl
Cl
Cl
Cl
PCB 66
Process H
Process N
Cl
Cl
Cl
PCB 25
Cl
Cl
Cl
PCB 28
Process Q
Process Q
Cl
Cl
PCB 4
Cl
Cl
PCB 6
Process M
Process Q
Cl
PCB 1

Figure 7: Reductive dechlorination of PCB 105

1.2. Chirality

1.2.1. Introduction to Stereochemistry

Stereochemistry (from the Greek origin *stereos*, meaning solid) deals with the chemistry of three-dimensional molecules. The field of stereochemistry began with the discovery of plane-polarized light by Malus in 1809. Shortly thereafter, it was observed that plane polarised light could be rotated by quartz crystals (Biot, 1812). Biot also observed that some quartz plates could rotate the light in different directions by diffraction, and other organic solutions and liquids could also rotate plane-polarized light (Biot, 1815). Hershel (1822) observed a correlation between optical rotation and non-superimposible mirror image facets of quartz crystals.

Louis Pasteur was the first to extend this correlation to molecules, both in solid and in solution form, and was the first to separate crystals of (+)- and (-)-tartaric acid from a mixture of crystals. Pasteur used a lens to observe the incline of dissymmetric facets of the crystals, and separating them manually with a pair of tweezers (Pasteur, 1848). When the crystals were separately dissolved, one solution rotated polarized light to the left, and the other solution rotated polarized light to the right.

1.2.1.1. Enantiomers

Pasteur postulated that the ability of the molecules and crystals to rotate the polarized light in different directions was due to the occurrence of dissymmetry between the mirror images of the crystals (Pasteur, 1860). It followed that this dissymmetry must also occur on the molecular level, bringing about the difference in the crystal structures. The components of the mixture were termed "enantiomers" from the Greek *enantios*, meaning opposite and *meros* meaning part, referring to a molecular species. Substances that rotate polarized light in a clockwise manner are termed dextrorotatory, and given the prefix *d*- or (+). Substances that rotate polarized light in a counter clockwise direction are termed levorotatory, and are given the prefix *l*- or (-).

There are some drawbacks to this system of nomenclature, as *dl* notation does not give information regarding the absolute configuration of the molecule about its asymmetric center, or the number of asymmetric centres in the molecule. To remedy this, R/S notation is applied. When applying R/S convention, the four substituents about the chiral centre are ranked in priority according to Cahn-Ingold-Prelog (CIP) sequence rule conventions (Cahn et al., 1956). The ranking of substituents is dependent on the atomic number of the substituent bonded to the centre of asymmetry. Atoms of a higher atomic number have a higher priority. If two atoms have identical atomic numbers, as is the case with alkyl substituents, the next atom in the chain is ranked. Hence, in the case with alkyl substituents, longer-chain alkyl substituents have priority over shorter chains. Double and triple bonds are assigned priority according to Figure 9. Once the substituent priorities are assigned, the molecule must be viewed down the C-E bond from the side opposite the substituent with the lowest priority. If the arrangement of the remaining substituents is clockwise, then the prefix *R*- (for Latin *rectus*, meaning "right") is used. If the sequence of the remaining substituents is in a counter clockwise arrangement, then the prefix *S*- (for Latin *sinister*, meaning "left") is used.

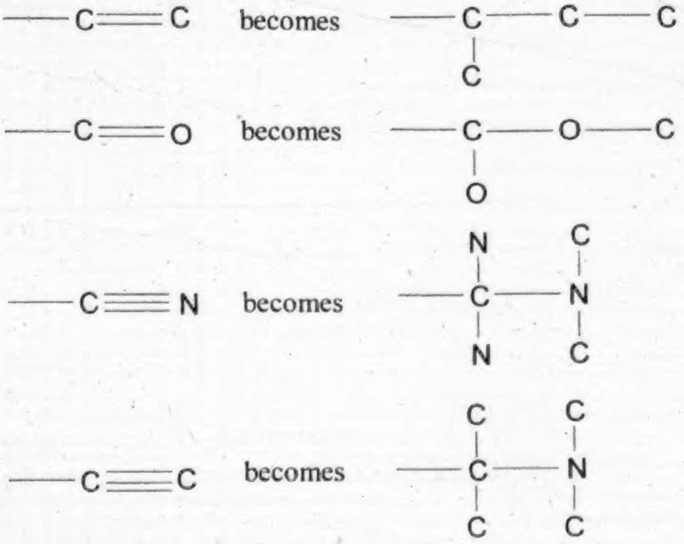

Figure 8: Assigning priority to double and triple bonds

1.2.1.2 Measuring Chiral Substances

A chiral compound consisting of a single enantiomer is termed "enantiomerically pure". A chiral compound containing equal concentrations of each enantiomer is called racemic. Because the rotation of plane polarized light occurs in opposite direction but in equal magnitude between (+) and (-) enantiomers, racemic mixtures do not rotate plane polarized light.

The relative concentrations of enantiomers are measured in two ways, enantiomer ratios (ERs) and enantiomeric fractions (EFs). The formulae for ER and EF is given in Equation 4, where (+) and (-) represent the areas of the (+) and (-) enantiomers, respectively. When the optical rotation of the enantiomers is unknown, E1 and E2 are used to represent the first and second eluting enantiomers, respectively (Equation 7, 8):

$$ER = \frac{(+)}{(-)} \qquad EF = \frac{(+)}{(+)+(-)}$$ **Equation 7**

$$ER = \frac{(E1)}{(E2)} \qquad EF = \frac{(E1)}{(E1)+(E2)}$$ **Equation 8**

Racemic mixtures have an ER equal to 1 and an EF of 0.5. Problems have arisen using ERs to measure enantiomeric composition due to the nonlinearity of the ratio scale. Specifically, ratios are unbounded and multiplicative, requiring transformations for standard mathematical operations, such as determining average values, whereas the fraction scale is bounded and additive, thus solving this problem (Ulrich et al., 2003). Enantiomerically pure substances have ERs of 0 for pure (-) enantiomer, infinity for pure (+) enantiomer. Because of this range, there is difficulty interpreting data graphically, as a unit change in one direction is not equivalent to a unit change in the other direction (Harner et al., 2000). This is the main reason for the development of the enantiomeric fraction (EF) (Harner et al., 2000). EFs may be calculated according to Equation 9. Using EFs, pure (+) and (-) mixtures have values of 1 and 0 respectively, with a linear distribution in between. Conversion between ER and EF may readily be performed using Equation 9. EF values present a more meaningful depiction of results, making it easier to observe the relative magnitude of enantiomeric depletion (Harner et al., 2000).

$$EF = \frac{ER}{1+ER} = \frac{1}{1+\frac{1}{ER}}$$ **Equation 9**

1.2.2. Chiral Molecules

1.2.2.1. Properties

The word "chiral" is derived from the Greek *kheir* meaning "handedness". Like hands, chiral compounds exist as non-superimposible mirror images of each other. Their chemical composition and connectivity are identical, but because of their properties, occupy a different three-dimensional area. A structural base for enantiomerism was independently proposed by van't Hoff and Le Bel in 1874. They described a molecule of the type Cabcd, that is a sp^3 hybridized carbon with 4 different substituents, as seen in Figure 10. Two non-superimposable arrangements are possible in this type of model.

Figure 9: C_{abcd}-type enantiomers

Cahn, Ingold, and Prelog (1956) expanded the theory of chirality, observing that any molecule lacking the three elements of symmetry – a plane of symmetry, a centre of symmetry, and an axis of symmetry – is chiral. Examples of symmetry are shown in Figure 11.

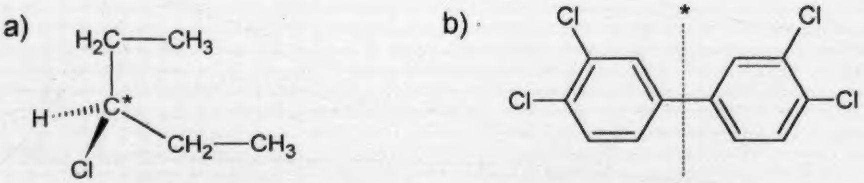

Figure 10: Center of symmetry (a) and plane of symmetry (b)

3-Chloropentane (Fig 11a) is not chiral, because the carbon point at the asterisk is not asymmetric, the molecule can rotate about this point, and as such will be superimposable on its mirror image. 2,3,2',3'-Tetrachlorobiphenyl (Fig 11b) is also not chiral, due to the mirror plane of symmetry indicated by the dotted line. Both molecules have an axis of symmetry, as indicated by the dotted line.

1.2.2.2 Effects of Enantiomers

The concept of chirality has significant importance to the environment, but also to industry. The pharmaceutical, agrochemical, and food industry each have chirality as a significant concern regarding the function and effectiveness of their products. Enantiomers of chiral compounds have identical physical and chemical properties when interacting with achiral environments. However, many environmental and biological environments are chiral. In the human body, all proteins are constructed with (*l*)-amino acids and (*d*)-carbohydrates. Theories regarding the enantiomeric homogeneity in organisms have been proposed, ranging from evolutionary enantiomer selection to suggestions that life originated after an enantiomeric excess was established (Bonner, 1988). This homogeneity creates an environment in the body that can potentially have different interaction kinetics with one member of an enatiomer pair.

Because organisms are a highly chiral environment, chirality is of great importance to the pharmaceutical industry. Enantiomers of chiral pharmaceuticals may have drastically different effects to the patient. Another example of the differing effects of chiral pharmaceuticals can be seen with ibuprofen. The (*R*)-enantiomer no effect while the (*S*)-enantiomer is an active analgesic (Buser et al., 1999). The differing effects of enantiomers in biological systems may also be extreme. The most common example of this is the case of thalidomide (Figure 12). Racemic thalidomide was prescribed in the 1950s and 1960s to pregnant women as a sedative. It was then found that while the (*R*)-enantiomer of the drug produced the effect of sedation, the (*S*)-enantiomer produced severe teratogenic effects, such as deformities in the arms (Blaschke et al., 1979). In some cases it is necessary to produce the pharmaceuticals in enantiomerically pure forms.

This is not the case for thalidomide, because the (*R*)-enantiomer is readily racemized in the body, producing the teratogenic (*S*)-enantiomer (Knoche and Blaschke, 1994).

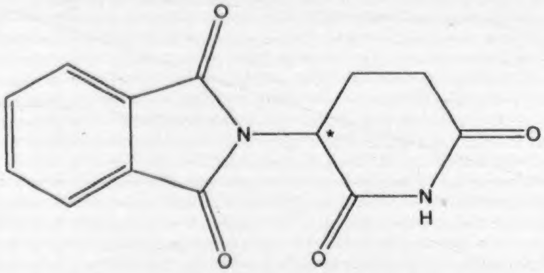

Figure 11: Thalidomide (* indicates chiral centre)

Interactions with chiral receptors in the body need not have such extreme consequences. Chirality concerns in the food industry relate to varying flavours of enantiomers. For example, the compound (*R*)-(+)-limonene exhibits the odor of oranges, while the (*S*)-(-)-limonene has a lemon odour. This perceptive difference arises from the differences in interaction of the limonene with the chiral olfactory receptors in the nasal cavity (Friedman and Miller, 1971). As is the case with pesticides and pharmaceuticals, differences arise not only in the perception and identity of the flavour, but the intensity of the flavour as well. In the case of nokotone, in which both enantiomers exhibit the odor of grapefruit, the (+)-enantiomer has an odor threshold of about 0.8 ppm. This threshold is approximately 750 times lower than that of (-)-nokotone (600 ppm) (Brenna et al., 2003).

Similar observations are made in the agricultural industry regarding the application of pesticides to crops. Enantiomers of some chiral pesticides may have different activities (Miyazaki et al., 1978). This concept has important ramifications to humans, because in this case, the desired effect for these compounds is a high toxicity. In the case of α-hexachlorocyclohexane (HCH), (+)-α–HCH is more toxic to (-)-α–HCH in rat cells (Huhnerfuss, 2000). Enantiomeric toxicities have also been found to differ between species. The chiral pesticides methamidophose and acetaphane were adminstred to houseflies (*Musca domestica*) and German cockroaches (*Blatella germanica*) (Miyazaki, 1997). With both pesticides, the (-)-enantiomer was observed to be more toxic to houseflies, and the (+)-enantiomer was observed to me more toxic to the German cockroach. Knowledge of the enantiomeric potency can help with the application of smaller quantities of pesticide, reducing the environmental load, and increasing application efficiency to target different species while reducing the hazard to non-target organisms (Miyazaki, 1997).

In addition to having different toxicities to organisms, enantiomers may also express different enzyme induction efficiencies (Hoekstra et al., 2001). CYP-type enzymes are a class of mixed function oxidases that are one of the main components of xenobiotic metabolism. There are hundreds of known CYP enzymes that have many different functions. One potential hazard with the induction of CYP enzymes is that while the xenobiotic causing the induction of the CYP enzyme may not be toxic, the enzyme may inherently make the xenobiotic, or other xenobiotics in the body significantly more toxic, bioactivating the xenobiotic.

1.2.3. Chiral PCBs

Biphenyl compounds do not have centers of asymmetry. However, chirality may still be observed due to atropisomerism. Atropisomerism is a condition of chirality based on an axis of symmetry. As mentioned previously in section 1.1.2, PCB congeners are unique arrangements of chlorine atoms about a biphenyl backbone. Of the 209 PCB congeners, 78 are axially chiral due to their asymmetric substitution about the two phenyl rings (Figure 13). However, these congeners are susceptible to rotation about the carbon-carbon biphenyl bond. The ease of rotation about this bond leads to unstable enantiomers, and racemization is observed. Nineteen of the 78 axially chiral PCBs have three or four chlorine atoms substituted in the *ortho* position (Figure 14) (Schurig et al., 1994; Hansen, 1999). A list of the stable chiral PCBs is given in Table 5.

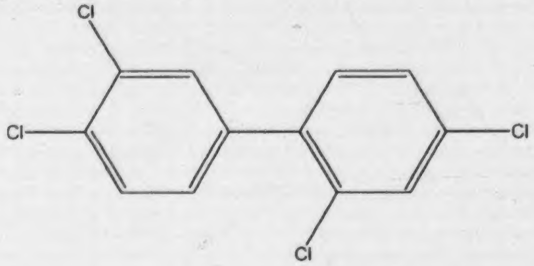

Figure 12: Asymmetric substitution of chlorine atoms about PCB 77

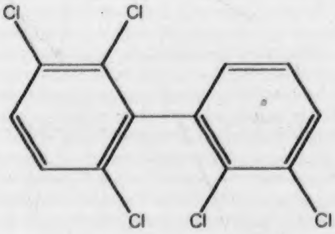

Figure 13: PCB 84 is rotationally stable due to three *ortho*-chlorines

Table 5: Stable atropisomers of chiral PCBs and their chlorine substitution patterns

IUPAC/BZ number	Chlorine position	IUPAC/BZ number	Chlorine position
45	236-2	144	2346-25
84	236-23	149	236-245
88	2346-2	171	2346-234
91	236-24	174	2345-236
95	236-25	175	2346-235
131	2346-23	176	2346-236
132	234-236	183	2346-245
135	235-236	196	2345-2346
136	236-236	197	2346-2346
139	2346-24		

The presence of these chlorine atoms sterically hinders rotation about the biphenyl bond, resulting in stable chiral enantiomers. The steric hindrance of rotation is termed atropisomerism. The free energy of rotation about the biphenyl bond is approximately 100-130 kJ mol^{-1} when three chlorine atoms are in the *ortho* position (Konig et al., 1996). The presence of an additional chlorine in the *ortho* position increases the free energy of rotation to approximately 180-247 kJ mol^{-1} (Konig et al., 1996; Harju and Haglund, 1999) making the polychlorinated biphenyl stable in its biplanar configuration at environmentally relevant temperatures for both tri- and tetra-*ortho* chlorinated biphenyls. The environmental aspects of chiral polychlorinated biphenyls will be discussed in greater detail in Section 1.4.

1.2.4. Enantioselective Processes

As previously mentioned, interactions between enantiomers of chiral compounds and chiral receptors may prefer one enantiomer to another. Because of this difference, many processes are inherently enantioselective. A selection of these processes will be discussed in this section.

1.2.4.1. EF Changes to Gauge Enantioselective Processes

A simple way to determine the occurrence of enantioselective processes is to observe the occurrence of any changes in the enantiomeric fraction (EF). For many studies of chiral pollutants, racemic mixtures are often the initial dose. Deviations from racemic EFs indicate that stereoselective processes are affecting one enantiomer preferentially. Alternatively, single enantiomers may be used, and separate studies undertaken on each enantiomer separately, with any differences in kinetics, reactivity, or toxicity noted.

1.2.4.1.1. Enantiomer Quantification

In order to determine the enantiomeric composition of a chiral substance, it is necessary to separate the enantiomers in order to quantify them. Techniques for enantiomer separation have significantly evolved since the first method of enantiomer separation by Pasteur in 1848, who manually separated crystals of tartaric acid into their enantiomers. Techniques for analytical separation are most commonly performed using capillary electrophoresis (CE), high performance liquid chromatography (HPLC), and gas chromatography (GC). Other techniques include supercritical fluid chromatography (SFC) and thin layer chromatography (TLC).

In order for chiral separation to occur using these techniques, there must be an element to the technique that discriminates between enantiomers of chiral compounds. For this reason chiral stationary phases (CSPs) or chiral selectors are used. It has been mentioned numerous times that chiral compounds have the potential to exhibit different kinetics when interacting with chiral substrates. For this reason, the chiral selectors used in these separation techniques are inherently chiral. These selectors include polysaccharides, proteins, and macrocyclic antibiotics. The polysaccharide cyclodextrin is one of the most common chiral selectors because of its modifiability, and ease of use (Schurig, 1994; 2001). Cyclodextrin consists of a number of a-d-glucopyranoside units linked to each other in a cyclic fashion through α-1,4 linkages. α-, β-, and γ-Cyclodextrins contain 6, 7, and 8 glucopyranoside residues, respectively (Figure 15). A detailed discussion of chiral separations is found in Section 1.3.

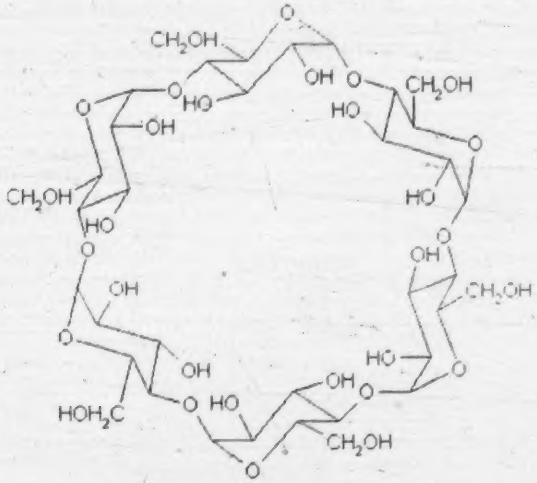

Figure 14: α-Cyclodextrin

1.2.4.2. Biotransformation

Biotransformation is the term given to the process of biochemically changing the properties of xenobiotics to improve their removal from an organism's body. This is accomplished by adding a polar functional group to the xenobiotic. Biotransformation of xenobiotics by organisms can be enantioselective, because the enzymes involved in metabolism are chiral. Likewise, the formation of metabolites also occurs enantioselectively. Numerous reports have been published reporting enantioselective biotransfomation of polychlorinated biphenyls in various animals. Blue mussel (*Mytilus edulis*) and eider duck (*Somateria mollissima)* samples were taken from the German Bight and analyzed for α-HCH using chiral gas chromatography. While near racemic ERs were observed in mussels (Pfaffenberger et al., 1992), ERs of eider duck livers reached infinity. This indicates the potential for total enantiomeric enrichment of (+)-α-HCH (Kallenborn et al., 1991).

Biotransformation of chiral pollutants varies between species. Enantiomeric composition of α-HCH in various organisms varies in the direction and magnitude of enantiomeric enrichment. Biotransformation of α-HCH has been observed to be variable in zooplankton, Arctic cod (*Arctogadus glacialis*), sea birds and ringed seal samples (Moisey et al., 2001). Similar observations were made by Fisk et al (2002) of α-HCH, cis- and trans-chlordane, oxychlordane and heptachlor epoxide in ringed seal blubber, providing evidence of differential biotransformation pathways between organisms for different types of chiral pollutants (Fisk et al., 2002). Biotransformation pathways have also been observed to differ between tissues of a single species (Wiberg et al., 1998).

Similar observations have been made for polychlorinated biphenyls. Enantiomeric composition studies suggest blue mussels (Huhnerfuss et al., 1995) have the ability to enantioselectively biotransfom chiral PCBs. Nonracemic EFs have also been observed in sharks (Blanch et al., 1996), cetaceans (Hoekstra et al., 2002), as well as various birds and mammals (Thomas et al., 1998; Fisk et al., 2001; Chu et al., 2003; Chu et al., 2003; Hoekstra et al., 2003; Wong et al., 2004; Warner et al., 2005). It is generally accepted that higher level consumers have higher biotransformation rates, as indicated by greater enrichment of enantiomers of chiral pollutants. In order to more accurately determine if biotransformation is occurring, it is necessary to undertake controlled *in vitro* experiments, or to determine predator-prey relationships in the food web, in order to determine if the nonracemic ratios of chiral pollutants are as a result of the organisms capacity to biotransform the xenobiotic, or uptake of nonracemic pollutants from its diet. Food web studies will be discussed in greater detail in Sections 1.3 and 1.4. Birds and mammals have a greater capacity than fish to biotransform chiral PCBs as indicated in the Northwater Polynya (NOW) food web (Warner et al., 2005). Fish also have the capatity to enantioselectively biotransform pollutants as indicated by Vetter et al. (2001) in mummichogs, and Wong et al. (2002b) in rainbow trout, using *in vitro* dosing of fish with racemic organochlorine pollutants, in order to show that lower level consumers have the ability to biotransform chiral POPs.

It was previously thought that invertebrates did not have the ability to stereoselectively biotransform persistent organic pollutants, indicated by racemic EFs of HCH, chlordane and PCBs observed in previous studies (Moisey et al., 2001; Hoekstra et al., 2002; Borga et al., 2005; Warner et al., 2005). Limited enatiomeric enrichment of chiral OCs have observed in the invertebrates such as *Mysis relicta* in Lake Superior (Wong et al., 2004), and macrozooplankton in Arctic marine waters (Borga et al., 2005). Warner and Wong (2006) have since shown that *Mysis* can stereoselectively biotransform polychlorinated biphenyls and chlordane. Further discussion of stereoselective biotransformation in food webs can be found in Section 1.4.

1.2.4.3. Biodegradation

Biodegradation is a significant vector for the removal of persistent organic pollutants from ecosystems. Decreasing concentrations of POPs have been observed in various matrices from different parts of the world. This degradation can be attributed to degradation by microorganisms. Bacteria and fungi present in water, soil and sediment may degrade chiral OC pollutants stereoselectively. Like organisms higher in the food web, there is much variation in degradation rates of enantiomers between different compounds and microorganisms. Nonracemic ratios of chiral pollutants have been observed *in situ* (Benicka et al., 1996). These observations were attributed to possible stereoselective microbial reductive degradation. To determine the occurrence of enantioselective microbial degradation, laboratory studies use controlled parameters under varying conditions. Ludwig et al. (1992) have studied the degradation of α–HCH, which was observed to be enantioselective. Degradation of this nature has been shown to be the case for microbial degradation studies of polychlorinated biphenyls under aerobic (Singer et al., 2002) and anaerobic (Pakdeesusuk et al., 2003) conditions, using laboratory microcosms. Differences in the degradation rates of enantiomers of α–HCH by microorganisms have been reported (Huhnerfuss et al., 1993). α–HCH has also been observed to degrade enantioselectively in lakes, bays and watersheds (Falconer and Bidleman, 1994; Bidleman et al., 1998).

1.2.4.4. Other Enantioselective Processes

Any interaction between a chiral molecule and a chiral receptor has the potential to occur in an enantioselective manner. One example of an interaction of this manner is the transport of chiral pollutants across the blood brain barrier. The active transport across the blood brain barrier is mediated by chiral proteins. Significant enrichment of (+)-α-HCH has been observed in the brain tissue of seals (*Pusa hispida*) (Moller et al., 1994), eider duck (Kallenborn et al., 1991) and roe deer (*Capreolus capreolus*) (Pfaffenberger et al., 1994). This transport has been observed to be almost completely enantioselective, as nearly enantiomerically pure (+)-α-HCH is seen in the brain tissue of the eider duck. Similar results suggesting differential transport of α-HCH across the blood brain barrier have been shown to occur in rats *in vivo* (Ulrich et al., 2001). Any transport across cell barriers that is mediated by proteins has the potential to be enantioselective. Passive diffusion across membranes, a process reliant on physical conditions, is not enantioselective.

1.3. Chiral Separations by Gas Chromatography

In order to determine the enantiomeric composition of chiral pollutants, enantiomers must be individually quantified. For this to take place, chiral separations must occur. Enantioseparation was first accomplished by Gil-Av et al. in 1966, who used amino acid derivatives as a stationary phase to separate enantiomers of amino acids (Gil-Av and Feibush, 1967). Current methods exist for the separation of enantiomers using analytical techniques such as gas chromatography (GC), liquid chromatography (LC), and capillary electrophoresis (CE), supercritical fluid chromatography (SFC), and thin-layer chromatography (TLC). GC, HPLC, and CE are the most frequently used techniques. Separations occur as equilibrium is established between two phases, a stationary phase and a mobile phase. Analytical separation is achieved when different components become associated with either phase more efficiently than the other.

Because the PCBs analyzed in this thesis are semi-volatile, this section will focus specifically on chiral GC techniques.

The analytical separation of molecules is accomplished by exploiting differences in the mobility of molecules between two phases. The retention of molecules in analytical chemistry is characterized by their retention coefficient *k*, which is calculated using Equation 10:

$$k_i = \frac{C_{i,s}}{C_{i,m}}$$

Equation 10

where $C_{i,s}$ is the concentration of a compound *i* associated with the stationary phase of a system and $C_{i,m}$ is the concentration of *i* associated with the mobile phase. The retention coefficient *k* may be calculated using observed data if an unretained compound is also introduced into the system (Equation 11): where t_r is the retention time of the analyte, and t_0 is the retention time of an unretained component, also referred to as the void volume in HPLC:

$$k_i = \frac{t_{r,i} - t_0}{t_0}$$

Equation 11

Separation is achieved when the retention factors of two substances differ, and is illustrated by the separation factor α (Equation 12), where k_j is the retention factor of the more strongly retained molecule:

$$\alpha_{j/i} = \frac{k_j}{k_i} = \frac{t_{r,j} - t_0}{t_{r,i} - t_0}$$

Equation 12

The degree of separation between two components is described by the resolution, *Rs* (Equation 13), where w_i and w_j are the peak widths of the two components at the peak base:

$$Rs = \frac{t_{r,j} - t_{r,i}}{\frac{1}{2}(w_j + w_i)}$$ **Equation 13**

The efficiency of a column is described by the number of theoretical plates (*N*), as calculated from Equation 14:

$$N = 16\left(\frac{t_{r,i}}{W_i}\right)^2$$ **Equation 14**

A “plate” is a theoretical unit of an analytical technique where separation occurs. Larger values of *N* indicate a column has higher separation efficiency, and can separate more complex mixtures (Skoog et al., 1998).

In order for enantiomeric separation to occur, there must be an interaction occurring with a phase that is preferential to one enantiomer over the other (Yashima and Okamoto, 1995). To facilitate this, chiral selectors are introduced to the techniques. Separations of enantiomers of chiral analytes are most frequently performed by GC and HPLC. The mechanisms of enantioseparation in these techniques are similar, exploiting the knowledge that enantiomers interact with different affinities to chiral substrates.

Gas chromatography is a technique that uses a gaseous mobile phase to elute analytes. The carrier gases most frequently used as mobile phases in GC are high purity hydrogen, helium, and nitrogen. Van Deemter curves of these gases are given in Figure 16. A disadvantage of using nitrogen as a mobile phase is its rapid decrease in efficiency at increasing mobile phase linear velocities. Hydrogen is ideal because of its high efficiency at higher linear velocities, however, safety concerns arise from using hydrogen as a carrier gas. Helium is the most preferred carrier gas, because of its efficiency at higher linear velocities and is safe and easy to use.

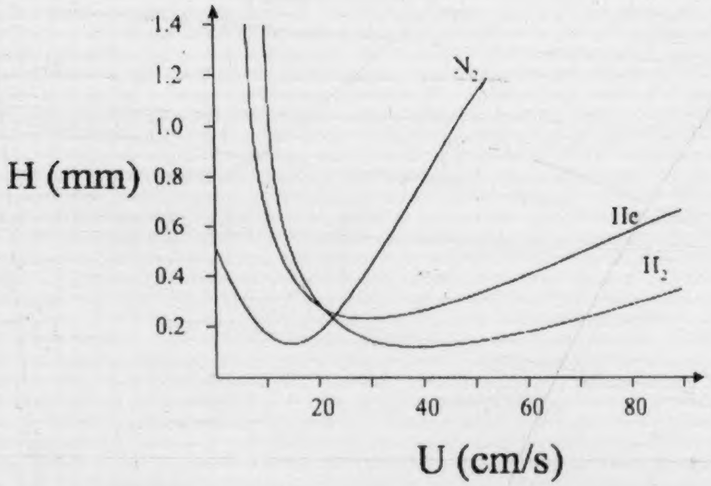

Figure 15: van Deemter curves for common carrier gasses in GC (Sacks et al., 1998)

Gas chromatography is the most preferred technique for the analysis of volatile environmental pollutants. Because the fused silica capillary columns used in GC are tens of metres long, very high plate numbers are achieved, and high resolution can be obtained. The separation of compounds in GC is governed by temperature and interactions of the analyte with the stationary phase. Separation of enantiomers is governed by the type of CSP in use.

There are a variety of CSP available to obtain enantioseparation on GC columns. The most common CSPs in use are cyclodextrin molecules and their derivatives (Li and Purdy, 1992). Cyclodextrins (CDs) are naturally occurring carbohydrates, and were observed to exist in three stable forms (Schardenger, 1911). CDs are cyclic polysaccharides consisting of varying numbers of D-(+)-glucopyranose units linked by (α)-1,4 carbohydrate bonds (Figure 15) (Schardenger, 1911). α-, β-, and γ-cyclodextrin consist of 6, 7, and 8 glucopyranose units, respectively. The saccharide units of the cyclodextrin molecule are arranged such that the hydroxyl groups on the 2 and 3 positions of the oligosaccharide are arranged at one end, and the hydroxyl groups on the 6 position of the glucopyranose are on the opposite side. This arrangement forms a cavity with a hydrophilic mouth and a slightly hydrophobic core. Increasing the number of D-(+)-glucopyranose units increases the volume of this cavity, and therefore the type of enantiomer separations possible.

Enantiomer separations using CDs as chiral stationary phases occurs by forming inclusion complexes with a variety of chiral analytes (Hamilton and Chen, 1988; Lipkowitz and Stoehr, 1996). The stabilities of the complexes formed depend upon several interactions such as hydrogen bonding, dipole-induced dipole interactions, and pi-pi forces (Lipkowitz and Stoehr, 1996). Because the CD stationary phase is made up of chiral saccharide units, enantiomers of chiral compounds reversibly interact with the CD with different kinetics, giving rise to enantiomeric separation. Often, one enantiomer exhibits a weak molecular association with the CD, while the other enantiomer is excluded due to steric hinderance, thus producing a high selectivity factor (Schurig and Nowotony, 1990).

Initial studies using chiral GC involved the binding of CD stationary phases to various solid supports (Harada et al., 1978; Zsadon et al, 1983; Schurig, 1994), however, preparation of these CSPs was a tedious process and exhibited low stability and enantiomeric separation efficiency. This problem was resolved by linking CSPs to polysiloxanes with alkyl spacers of varying length, thus improving temperature stability, efficiency and robustness. In addition, the chiral polysiloxane (Chirasil) CSPs may be immobilized on the inner walls of fused silica columns, to serve as a bonded chiral stationary phase. Modified cyclodextrin CSPs can be linked to polysiloxanes producing Chirasil-Dex type CSPs (Fischer et al., 1990; Schurig et al., 1991).

CD stationary phases may also be derivatized in order to optimize the separation of a number of chiral substrates, and was a major advancement in the field of chiral analysis. By regioselectively inserting different functional groups onto the hydroxyl functionalities on the CD, a wide range of derivatives can be formed (Snopek et al., 1996). Modified CD stationary phases gave been used for enantiomeric analysis in many different fields, such as flavour chemistry (Mosandl, 1995; Bicchi, 1992), clinical analysis (Heil et al., 1998), and the analysis of chiral organochlorine pollutants, such as PCBs (Vetter and Schurig, 1997; Vetter et al. 1997, Wong and Garrison, 2000). There are other chiral selectors that may be used to separate enantiomers. Amino acids, chiral metal co-ordination compounds, and crown ethers have been used to facilitate the separation of enantiomers of various racemates (Schurig, 2002).

Because separation of compounds in GC is dependent on the vapour pressure of the analyte of interest, techniques are limited to the analysis of volatile and semivolatile compounds. In order to increase the number of types of compounds that can be separated by GC, chemical derivitization is employed to increase the volatility of compounds in order to use GC. GC is ideal for the analysis of organochlorine pollutants, because of its ability to be linked to highly sensitive and selective detectors such as electron conductivity detectors (ECD) and mass spectrometry (MS).

1.4. Food Web Dynamics

1.4.1. Introduction

In order to determine the fate of persistent organic contaminants in the environment, it is important to study the food chains of the ecosystem of interest. Constituents of the food web, predator-prey relationships, and population analysis can affect the flow of xenobiotics to the top of the food chain (Muir et al., 1995; Wong et al., 2001a). Food web analyses can be used to assess the accumulation and elimination of POPs, and ultimately, the potential for human exposure, as humans are at the top of many food chains.

1.4.1.1. Structure

In order to determine the structure of a food web, several methods are applied. The simplest way to gauge the structure of a food web is to use diet analysis, i.e., record the stomach contents of each consumer of the food web and determine the predator-prey relationships. In the past, trophic levels have been expressed in discrete terms, such as "producers", "primary consumers", "secondary consumers", and so on up to "top predator". Determination of trophic level may be performed by calculation, based on these discrete trophic levels and the composition of an organism's diet (Miller, 1978).

The use of this quantized scale is inaccurate and problematic (Broman et al., 1992). Difficulties arise when analyzing food web constituents above the level of "primary consumer", as all levels above are considered "intermediate", as it is rare for an organism to consume solely a single food source. In order to more accurately model food webs on a scale that is not quantized, stable isotope analysis is performed.

1.4.1.2. Stable Isotope Analysis

In the mid-1980s, it was discovered that isotopic signatures of nitrogen and carbon varied between food web constituents. Peterson et al. (1985) used the isotopic signatures of ^{15}N and ^{13}C to gauge the flow of organic matter though a food web. The ratio of the heavier to the lighter stable isotopes of nitrogen increases with trophic position in food chains, due to slower kinetics of the heavier isotope, presenting an ideal variable with which to assess trophic level (Fisk et al., 2001a; Fisk et al., 2001b; Hobson et al, 1995; Michner and Schnell, 1994). The ratio of the heavier to the lighter isotopes of carbon indicates the flow of organic carbon throughout a food chain, which may be used as an indicator for predator-prey relationships (Hobson et al., 2002). Because the ratio of ^{14}C to ^{13}C is generally not enriched with trophic position in the food web (Hobson and Welch, 1992), this isotope ratio is used to gauge the food sources of the food web constituents (Hobson et al., 1995, Borga et al., 2005). Isotopic ratios of carbon are also enriched in benthic or inshore food webs compared to pelagic food webs (Hobson and Welch, 1992a; Hobson et al., 1994).

Stable isotope ratios are expressed in terms of δ^{15}N and δ^{13}C in parts per thousand, which are calculated according to Equations 15 and 16:

$$\delta^{15}N = \left[\frac{\left({}^{15}N/{}^{14}N\right)_{Sample}}{\left({}^{15}N/{}^{14}N\right)_{Std.}} - 1\right] \times 1000$$

Equation 15

$$\delta^{13}C = \left[\frac{\left({}^{13}C/{}^{12}C\right)_{Sample}}{\left({}^{13}C/{}^{12}C\right)_{Std.}} - 1\right] \times 1000$$

Equation 16

$^{15}N/^{14}N_{std.}$ values are based on isotopic measurements of atmospheric nitrogen, and $^{13}C/^{12}C_{std.}$ are based upon isotopic measurements of Pee Dee Belemnite, a standard material.

Calculation of trophic position is often done in reference to an organism of known trophic position. In marine ecosystems, *Canalus hyperboreus*, an invertebrate assumed to occupy trophic level 2 (primary herbivore) is often used as a baseline for trophic level calculation. Depending on the isotopic enrichment of ^{15}N between trophic levels in the food web, the calculation of trophic level may vary. By analysing the ratio of ^{15}N in primary consumers, and assuming that isotopic enrichment is constant among trophic levels, the trophic position may be calculated according to equation 17 (Hobson and Welch, 1992a). In order to apply this calculation to freshwater ecosystems, one must first know the ^{15}N signature of lake-specific commonly occurring primary consumers as a baseline, replacing *C. hyperboreus* in Equation 17 (Vander Zanden et al., 1997):

$$TL = 2 + \left(\delta^{15}N_{consumer} - \delta^{15}N_{c.hyperboreus}\right)/\delta^{15}N_{enrichment} \qquad \textbf{Equation 17}$$

1.4.2. Bioaccumulation

The term bioaccumulation refers to the degree to which a substance is preferentially taken up by an organism's tissues. The degree of bioaccumulation depends on several factors, such as the nature of the chemical and the metabolic capabilities of the organism. The property of a xenobiotic to bioaccumulate is dependent on its K_{ow}: or the ratio of concentrations of octanol and water in an octanol-water system that has reached equilibrium (Gobas, 2001). K_{ow} can be calculated according to Equation 18:

$$K_{ow} = \frac{C_o}{C_w} \qquad \textbf{Equation 18}$$

Where C_o and C_w refer to the concentrations of the chemical in the ocatnol and water phases, respectively. This is of great use, because the ability of a chemical to partition between the octanol-water phases accurately represents how a chemical will partition between the lipids of organisms and water (Gobas, 2001). In monitoring the accumulation of compounds into organisms using K_{ow}, it is useful to visualise the organism as a mass of octanol in direct contact with its environment. K_{ow} is usually given in base-10 logarithm values, and is usually stated as log K_{ow}.

Animals are complex vessels, containing fractions of proteins, lipids, carbohydrates, and other diverse organic materials (Schwarzenbach et al., 2003). This wide range of media exhibit varying degrees of polarity. Because PCBs are highly lipophilic, the lipid fraction of the tissue is of particular importance for the bioaccumulation of PCBs in an aquatic food web. Lipids serve as structural components and energy reserves in the body (Schwarzenbach et al., 2003). Because of this, the degree of lipid content can vary between organisms, and in between tissues. For the most part, lipid content measurements in aquatic biota vary between 10% and 30% lipid. Lipid content may also vary depending on growth phase and environmental conditions (Shirfin and Chisolm, 1981, Stange and Swackhamer, 1994).

The medium in which an organism lives has a significant effect on the bioaccumulation of PCBs. Bioaccumulation describes the net result of all uptake and elimination factors taking place. For example, animals may uptake contaminants passively from the air or water, in addition to uptake via ingestion of sorbed molecules in sediment or present in the diet (Schwarzenbach et al., 2003). Passive uptake is termed bioconcentration, whilst the uptake via ingestion of sediment or diet is termed biomagnification.

1.4.3. Bioconcentration

Bioconcentration refers to an organism's ability to uptake a chemical from its environment. In an aquatic food web, this refers to the ability of an organism to uptake chemicals from the water and its ability to eliminate these chemicals. A balance is formed between the rate of accumulation via gills and/or skin, and the loss of these chemicals via gills, fecal elimination, and metabolic transformation (Gobas and Mackay, 1987; Kawano et al., 1988; Campfens and MacKay, 1997; Gobas and Morrison, 2000). The degree to which a chemical is bioconcentrated is expressed by its bioconcentration factor, given by BCF, which is the ratio of the chemical's concentration in an organism, compared to the concentration in water, as expressed by Equation 19:

$$BCF = \frac{C_{i,org}}{C_{i,water}} \qquad \textbf{Equation 19}$$

where $C_{i,\,org}$ is the concentration of a chemical in the organism and $C_{i,water}$ is the concentration of the chemical in water.

Often, chemicals with a high log K_{ow} may sorb to particulate and organic material in the water column, reducing its bioavailability. When a chemical sorbs to particulate and organic material, the free concentration in the water column is decreased, reducing the fraction of the chemical that can be readily absorbed by aquatic organisms. Because of this, the BCF of a chemical is more accurately represented by the ratio of chemical concentration in an organism to the freely dissolved concentration of the chemical, as in Equation 20.

$$BCF = \frac{C_{i,org}}{C_{i,dissolved}} \qquad \textbf{Equation 20}$$

The relationship between Kow and BCF is usually correlated, and linear relationships may be applied to predict the BCF of a persistent organic pollutant in an ecosystem. The theory behind this assumes that the bioconcentration process is essentially a partitioning process between the water and the organism (Hamelink et al., 1971; Veith et al., 1979). The model for this type of analysis views an organism as a mass of lipid in equilibrium with the water surrounding it (Mackay, 1982). Therefore the Kow may be used to assess bioconcentration (Gobas and Mackay, 1987), normalized to the lipid content of the organism.

1.4.4. Biomagnification

Bioaccumulation may be assessed using a bioaccumulation factor, which may be calculated by Equation 21:

$$BAF_i = \frac{C_{i,organism}}{C_{i,med}} \qquad \textbf{Equation 21}$$

where $C_{organism}$ is the actual concentration of the contaminant in the organism and C_{med} is the concentration in the media in which the organism lives. In aquatic systems, C_{med} is the concentration of contaminant dissolved in the water (i.e., not including the fraction sorbed to suspended particulate matter or dissolved organic materials) (Schwarzenbach et al., 2003)). When modelling for bioaccumulation, it is useful to simplify the processes occurring in an organism as first order processes that occur (Gobas and Morrison, 2000). These rates vary depending on the type of organism, and the type of pollutant. Some of these processes in fish are illustrated in Figure 17.

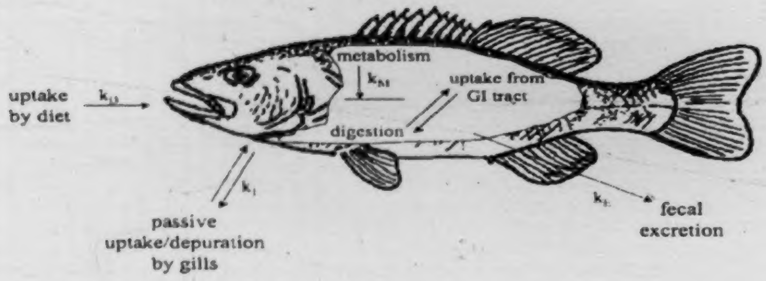
metabolism
k_M
uptake from GI tract
uptake by diet
k_D
digestion
k_1
passive uptake/depuration by gills
k_E
fecal excretion

Figure 16 : Uptake and Elimination Processes in Fish , adapted from Schwarzenbach et al. (2003)

In addition, the lipid content of an organism may vary over time, depending on its life phase (Henderson and Tocher, 1987), and an organism's growth is also not constant over time, so the values for k_g do not remain constant (Schwarzenbach et al., 2003). Despite these assumptions, this model is useful to understand the processes affecting the observations made from field measurement.

1.4.5. PCB 153 Analysis

A common method of modeling the bioaccumulation of persistent organic pollutants in a food web is to measure the concentrations of PCB 153. PCB 153 is considered one of the most recalcitrant and bioaccumulative PCB congeners, frequently having the highest concentrations measured in biota (Muir et al., 1998). PCB 153 is also commonly used as a marker for assessing the potential biomagnification and bioaccumulation of other persistent organic pollutants (Boon et al., 1994).

PCB 153 is lipophilic, and very resistant to metabolism. The differences in metabolism of PCB 153 among species are negligible. Because of this, species differences do not affect the relationships between the concentration of PCB 153 and trophic position. A strong positive correlation between the lipid-corrected concentration of PCB 153 and the $\delta^{15}N$ ratio confirms the occurance of biomagnification through a food web (Muir et al., 1988). When assessing biomagnification in this manner, it is useful to limit the measurement of this contaminant to male organisms, because there are elimination pathways in females (excretion through milk, laying eggs) that may significantly reduce observed concentrations.

Chapter 2 - Enantiomeric Fractions of Chiral PCBs in Standard and Certified Reference Materials[1]

2.1. Introduction

The analysis of chiral compounds in the environment is an area of emerging significance, because many biological processes can be enantioselective (Huhnerfuss et al., 1993). Many chiral, persistent, organochlorine compounds (OCs) are released into the environment as racemic mixtures. Enantiomers of chiral compounds exhibit identical chemical and physical properties, with the exception of the direction of rotation of a plane of polarized light, and their reaction rates with other chiral or prochiral substrates. Enzymes may interact in a preferential manner with one enantiomer over the other (Williams, 1996). Because of the kinetic differences between enantiomers, changes in the enantiomeric fractions (EFs) of chiral OCs may be indicative of the occurrence of biological processes such as microbial reductive dechlorination (Pakdeesusuk et al., 2003) and biotransformation within living organisms (Borga and Bidleman, 2005; Warner et al., 2005).

It is known that enantiomers of chiral OCs exhibit varying biological responses, such as activity (Miyazaki et al., 1978), metabolic pathways (Vetter et al., 2001; Fisk et al., 2002), and toxicities (Hoekstra et al., 2001). Because of these differences, analyses of chiral OCs in various environmental matrices have become relevant issues in analytical chemistry and risk assessment. As a part of these studies, reference materials are an integral component of quality assurance/quality control protocol (Robson and Harrad, 2004; Kurt-Karakus et al., 2005). Current methods for chiral OC analysis employ a number of extraction and cleanup procedures and analytical techniques, such as gas chromatography (GC) (Jaus and Oehme, 1999; Wong and Garrison, 2000)), comprehensive two-dimensional gas chromatography (GC×GC) (Bordajandi et al., 2005), and liquid chromatography (LC) (Champion et al., 2004). While the pollutant composition of many reference materials have been extensively quantified, there is little data on the enantiomer composition of such materials, with a few exceptions (Wong et al., 2002). Here we report the enantiomer composition of additional Standard Reference Materials (SRMs) often used for OC analytical method development and quality assurance/quality control. Although our findings are not certified values, we hope that they will nonetheless be useful for these purposes.

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[1] A version of this chapter has been published. Morrissey et al. Chemosphere **66**(2): 326-331.

2.2. Experimental

The chiral PCB congeners 91, 95, 136, 149, 174, and 183 were selected for analysis based on their presence in the environment, as well as their ability to be separated by chiral GC (Wong and Garrison, 2000). Standard Reference Materials analyzed were obtained from the U.S. National Institute of Standards and Technology (NIST): SRM 1939A (PCBs in Hudson River Sediment, n=4) (Rebbert et al., 1992), SRM 1946 (Lake Superior Fish Tissue, n=6) (Poster et al., 2003), and SRM 2978 (Mussel Tissue, Raritan Bay, NJ, n=6).(Poster et al., 2004). These reference materials were selected based on their relevance for environmental studies to be representative of varying matrices as a part of quality analysis and quality control practices. Reference materials CRM EC5 (Lake Ontario Sediment from Environment Canada) and NIST SRM 1945 (Organics in Whale Blubber) were run concurrently with selected SRMs to serve in quality assurance/quality control (Wong et al., 2002). It must be noted that SRM 1945 is a restricted material by the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES), and requires import permits for entry into Canada.

2.2.1. Sample Extraction Procedure

All samples were homogenized using a mortar and pestle with anhydrous sodium sulfate (Tracepur ACS-grade, EMD Chemicals, Gibbstown, NJ). Sodium sulfate was ashed at 550 °C for three hours to remove trace organic contaminants prior to use. Surrogate standards of PCB 30 and 204 (Accu Standard Inc. New Haven, CT) were added to all samples prior to extraction. Samples were extracted with pesticide-grade dichloromethane (DCM) in a Soxhlet apparatus for 16 hours, filtered through a bed of anhydrous sodium sulfate, and concentrated using a rotary evaporator. Lipid percentage was determined by mass difference using a small aliquot of the concentrated extract (~10%). Gel permeation chromatography using 200-400 mesh SX-3 Biobeads (Bio-Rad Laboratories, Hercules CA), with 1:1 DCM:hexane as a mobile phase was used to remove lipids and large biological materials from the extracts of biological material. Extracts were solvent exchanged into hexane and concentrated to 1 mL. Column chromatography using 3% by weight deactivated silica gel (70-270 mesh, Aldrich Chemicals, Fair Lawn, NJ) and 8.5% by weight deactivated aluminum oxide (150 mesh, Aldrich Chemicals, Fair Lawn, NJ) was used to separate the extract into two fractions. Fraction 1 (F1) containing PCBs was collected using 30 mL of hexane, and fraction 2 (F2) containing the remainder of chlorinated pesticides was collected using 5% acetone in hexane (Foreman et al., 1995). Sulfur was removed from sediment samples using activated copper (Sigma-Aldrich Inc. St. Louis, MO). Extract fractions were concentrated to approximately 200 μL using a nitrogen evaporator and fortified with PCB 166 (Accu Standard Inc. New Haven, CT) as an internal standard.

2.2.2. Chiral Analysis

Chiral PCB enantiomers were quantified using a HP 5890/5971 gas chromatograph/mass selective detector using electron impact ionization (70 eV) in selective ion monitoring mode. The three most abundant ions of the molecular ion cluster (e.g., m/z 358, 360, and 362 for hexachlorobiphenyls) were used for detection. A collection of chiral columns was used to obtain data for target chiral PCB enantiomers. PCBs 91, 95 and 136 were quantified using a Cyclosil-B column (30 m × .25 internal diameter (i.d.) × 0.5 μm film thickness (df), J&W Scientific), while PCBs 91, 95, 136, 149, and 174 on a Chirasil-Dex column (30 m × .25 mm i.d. × 0.5 μm df, Varian, Walnut Creek, CA), and PCB 183 on BGB Column (30 m × .25 mm i.d. × 0.18 μm df, BGB Analytik, Adliswil, Switzerland) as previously described (Wong et al., 2002a). Enantiomeric fractions (EFs) (Harner et al., 2000) were calculated according to equations 7 and 8 on pages 40 and 41. Areas of (+) and (-) enantiomers were used where enantiomer elution order is known (PCBs 136, 149, 174) (Haglund and Wiberg, 1996; Wong et al., 2002a). Where the enantiomer elution order was unknown, areas of first eluting enantiomer (E1) and second eluting enantiomer (E2) were used. Racemic enantiomer distributions have an EF of 0.5, whereas EFs of 0 or 1 indicate pure single enantiomers of (-) or (+), respectively. Elution orders of enantiomers on the columns used are described elsewhere (Wong and Garrison, 2000). A 95% confidence interval of ±0.032 from measured racemic (EF=0.500) standards was used for statistical comparisons of sample EFs compared to racemic standards (Wong et al., 2004).

Extraction blanks were run with every extraction set and processed identically to SRMs analyzed; no target analytes were detected in blanks.

2.3. Results and Discussion

Chiral PCBs were successfully identified. Retention times (Table 6) for chiral enantiomers are reported relative to PCB 166 internal standard. Lipid percentages of biota samples were consistent with certified values. Concentration values reported (Table 7) are a combination of certified values reported in certificates of analysis, and recovery-corrected concentrations determined from our measurements. Variation in EFs between replicate samples of each SRM was low (<2% relative standard deviation), indicating that the measurement of EFs from studied SRMs is highly reproducible (Wong et al., 2002). Concentration measurements of chiral OCs were consistent with reported PCB concentrations of naturally contaminated biota (Huhnerfuss et al., 1995; Benicka et al., 1996; Gerstenberger et al., 1997). Concentrations and EFs of chiral PCBs in CRM EC-5 and SRM 1945 quality control samples were consistent with values reported in Wong et al. (2002a). Concentrations of PCB 95 and PCB 183 in SRM 1945, and PCB 183 in CRM EC-5 were consistent with certified concentrations. Extraction blanks all measured non-detectable concentrations of target chiral PCBs.

Table 6: Substitution patterns and relative retention times of chiral PCB atropisomers of this study

PCB atropisomer		Relative retention time[a]	
IUPAC no.	Substitution	E1	E2
91	236-24	0.643[c], 0.694[d]	0.647[c], 0.691[d]
95	236-25	0.617[c], 0.674[d]	0.623[c], 0.677[d]
136[b]	236-236	0.744[c], 0.781[d]	0.741[c], 0.777[d]
149[b]	236-245	0.804[c]	0.799[c]
174	2345-236	0.895[c]	0.903[c]
183	2346-245	0.964[e]	0.967[e]

[a] Relative to PCB 166 (2,3,4,4',5,6,-hexachlorobiphenyl) internal standard

[b] Enantiomers expressed as (+) and (-)

[c] Relative retention on Chirasil-Dex column

[d] Relative retention on Cyclosil-B column

[e] Relative retention on BGB column

Table 7: Concentrations (ng/g dry weight for SRM 1939a; ng/g wet weight for SRMs 1946 and 2978) and EFs of Chiral PCBs in SRMs of this study. (Number of samples studied in parentheses).

SRM 1939a: PCBs in Hudson River sediments (n=4)

Compound	Concentratio	EF	EF Range
PCB 91	304 ± 7	0.507 ± 0.001	0.507 - 0.509
PCB 95	1210 ± 420	0.394 ± 0.027	0.378 - 0.424
PCB 136	84.4 ± 2.7	0.543 ± 0.004	0.538 - 0.546
PCB 149[a]	427 ± 47	0.610 ± 0.003	0.607 - 0.612
PCB 174	51.1 ± 2.1	0.583 ± 0.004	0.579 - 0.586
PCB 183[a]	47.3 ± 2.3	0.463 ± 0.008	0.458 - 0.472

SRM 1946: Lake Superior lake trout (n=6)

Compound	Concentratio	EF	EF Range
PCB 91	11.4 ± 1.3	0.146 ± 0.007	0.142 - 0.155
PCB 95[a]	3.5 ± 0.7	0.343 ± 0.009	0.336 - 0.356
PCB 136	1.4 ± 0.7	0.301 ± 0.014	0.281 - 0.316
PCB 149[a]	26.3 ± 1.3	0.424 ± 0.011	0.407 - 0.437
PCB 174	5.8 ± 1.9	0.552 ± 0.007	0.542 - 0.559
PCB 183[a]	21.9 ± 2.5	0.477 ± 0.007	0.472 - 0.488

SRM 2978: Mussel tissue from Raritan Bay, NJ (n=6)

Compound	Concentratio	EF	EF Range
PCB 91	2.0 ± 0.6	0.461 ± 0.009	0.448 - 0.464
PCB 95[a]	20.8 ± 2.1	0.522 ± 0.008	0.513 - 0.535
PCB 136	3.6 ± 0.9	0.475 ± 0.014	0.459 - 0.490
PCB 149[a]	34.73 ± 0.69	0.479 ± 0.009	0.466 - 0.488
PCB 174	ND	N/A	N/A
PCB 183[a]	5.25 ± 0.15	0.457 ± 0.003	0.455 - 0.460

[a] NIST Certified Concentration

2.3.1. SRM 1939A - PCBs in Hudson River sediments

Nonracemic EFs of NIST SRM 1939A were consistent with previously published studies of sediment from the Hudson River, indicating that stereoselective reductive dechlorination had occurred in the sediments there (Benicka et al., 1996). The EF of PCB 95 indicates enrichment of the second eluting enantiomer, which is in agreement with previous measurements of this congener in Hudson River sediment (Benicka et al., 1996; Wong et al., 2001). The EF values measured for SRM 1939A were quite similar to the range of EFs observed in an earlier survey of the Hudson (Wong et al., 2001a) for PCBs 91 (mean EF of 0.507, survey study EF range of 0.509-0.561) and PCBs 136 (mean EF of 0.543, survey range of 0.500-0.517). EFs of PCB 149 (mean EF of 0.610) and PCB 174 (mean EF of 0.583) were considerably higher than previously reported by Wong et al. , 2001a (ranges of 0.500-0.541 and 0.500-0.519, respectively). The EFs of PCB 95 (mean EF of 0.394) and PCB 183 (mean EF of 0.463) were somewhat lower than previously reported by Wong et al., 2001a (ranges of 0.440-0.481 and 0.494-0.505, respectively). However, several microbially-mediated dechlorination pathways exist in the Hudson (Bedard and Quensen, 1995) with different enantiomer preferences (Wong et al., 2001a). This observation indicates that the specific stereoisomer composition of sediments from Hudson River would depend on the location at which it was taken, as SRM 1939A was likely collected from different sites than that observed in the survey study. However, the PCB enantiomer composition observed in SRM 1939A is generally consistent with known stereoselective dechlorination activities in Hudson River sediments.

2.3.2. SRM 1946 - Lake Superior Lake Trout

The chiral PCB congener concentrations in NIST SRM 1946 were consistent with chiral PCB concentrations reported in previous food web studies on lake trout (*Salvelinus namaycush)* from Lake Superior (Kucklick and Baker, 1998; Wong et al., 2004). This is suggestive that trout in Lake Superior have the capacity to bioprocess chiral PCBs stereoselectively (Wong et al., 2002). Nonracemic EFs of PCBs 95, 136, and 174 (EFs of 0.359, 0.301, and 0.5521, respectively) fall near the median values of the study conducted by Wong et al. (2004). The EF of PCBs 91 (0.147) and PCB 149 (0.424) fall below the 25th percentile of the data in the previous studies of Lake Superior fish tissue. The samples collected for use in SRM 1946 and in the previous study by Wong et al. (2004) were both collected near the Apostle Islands (Poster et al., 2003). The observed differences from reported EFs may be due to variability between the specimens (mass, sex, age of individual fish) collected for SRM 1946, and those from the previous study. Nonracemic amounts of PCBs have been observed in many fish species, ranging from freshwater bass (*Micropterus salmoides*), bluegill (*Lepomis macrochirus*), suckers (*Catostomus commersonii*), and sculpins (*Cottus cognatus*) (Wong et al., 2001b), to Arctic cod (*Boreogadus saida*) (Warner et al., 2005). On the other hand, PCBs 95, 136, 149, and 174 were racemic in groupers (*Epinephelus marginatus*) (Serrano et al., 2000). These observations all indicate that enantioselectivity in biota is species-dependent. Nonracemic EFs may also indicate the occurrence of gender-dependent (Karlsson et al.) and age-dependent (Hoekstra et al. 2002) enantioselective processes in cod and in cetaceans, respectively. The observed EFs in SRM 1946 are consistent with the hypothesis that the highly nonracemic PCBs in Lake Superior lake trout are from a combination of *in vivo* biotransformation and uptake from prey. For example, the enrichment of (-)-PCB 136 in SRM 1946 is similar to that observed in rainbow trout (*Oncorhynchus mykiss*) that biotransformed the racemate in laboratory exposures (Wong et al., 2002b). Racemic PCB 95 was observed in that same study, consistent with field measurements suggesting that nonracemic PCB 95 in lake trout were due to uptake from sculpin, smelt, and cisco prey that all had similar enantiomer compositions (Wong et al., 2004).

SRM 2978 – Mussel Tissue From Raritan Bay, NJ

Concentrations of chiral PCB congeners in SRM 2978 are consistent with concentrations observed in SRM 1974a *Mytilus edulis* homogenate from Boston Harbor (Schantz et al. 1997), indicating similar degrees of contamination between Boston Harbor and Raritan Bay. SRM 1974a is no longer available for purchase. Racemic EFs were observed in SRM 2978, except for PCBs 91 (mean EF of 0.461) and 183 (mean EF of 0.457). The EF for PCB 91 is similar in magnitude to that observed for this congener in bivalves (*Corbicula* genus) in U.S. rivers (Wong et al., 2001b). Nonracemic PCB 183 was observed for *Corbicula* (mean EF= 0.355, Wong et al., 2001b) and for the marine species *Mytilus edulis* (EF range of 0.50-0.55, Huhnerfuss et al., 1995). The latter two studies measured PCB 183 enantiomers using different columns, so it is not clear if the enantiomer preference is the same as that in this study as elution order is unknown. The racemic EFs observed for the remaining congeners suggests that bivalves have little capacity to bioprocess chiral

PCBs stereoselectively (Huhnerfuss et al., 1995; Wong et al., 2001). It is likely that the nonracemic EFs observed were due to uptake of nonracemic contaminants from the diet, possibly from sediment, by these filter feeders. The slight differences between the EFs observed in SRM 2978 and those of previous studies may be due to differences between species analyzed (such as feeding patterns or diet) or also from different contaminant levels at the sites studied.

Chapter 3 - Chiral PCBs in the aquatic food web of Lac La Biche (LLB) Alberta, Canada

3.1. Introduction

Lac La Biche (LLB) is a large lake in northern Alberta, Canada (Figure 18) with a surface area of approximately 230 km^2 over three basins. The towns of Lac la Biche and Plamondon draw their drinking water from the lake, and discharge treated sewage into it. Recently residents have become concerned with the declining water quality in LLB as a result of its eutrophication, and nutrients and chemical contaminants entering LLB from anthropogenic sources. The overfishing of walleye (*Sander vitreus vitreus*) and lake whitefish (*Coregonus clupeaformis*) has also resulted in the proliferation of the forage fish population (Vander Zanden et al., 2005). In response to this, populations of double-crested cormorants (DCCO) (*Phalacrocorax auritus*) and other piscivorous birds have increased dramatically, nesting on the islands of LLB, primarily High Island and Pelican Island (Earle, 2006). Numbers of DCCO have become troublesome for local residents, resulting in population control measures for the DCCO of LLB, in addition to attempts to re-stock LLB with walleye, which have been unsuccessful (White and Rawles, 2006). The organisms of the LLB watershed have been contaminated with organic pollutants that have been deposited to the watershed. Studying the contamination of the LLB food web by chiral PCBs presents a unique opportunity to monitor the trophodynamics of chiral pollutants in the LLB aquatic food web. This study will serve as the basis for determining future changes in OC pollutant trends in the LLB watershed. Future studies will be used to monitor the potential changes in the trophodynamics of chiral pollutants in the LLB food web as it may change.

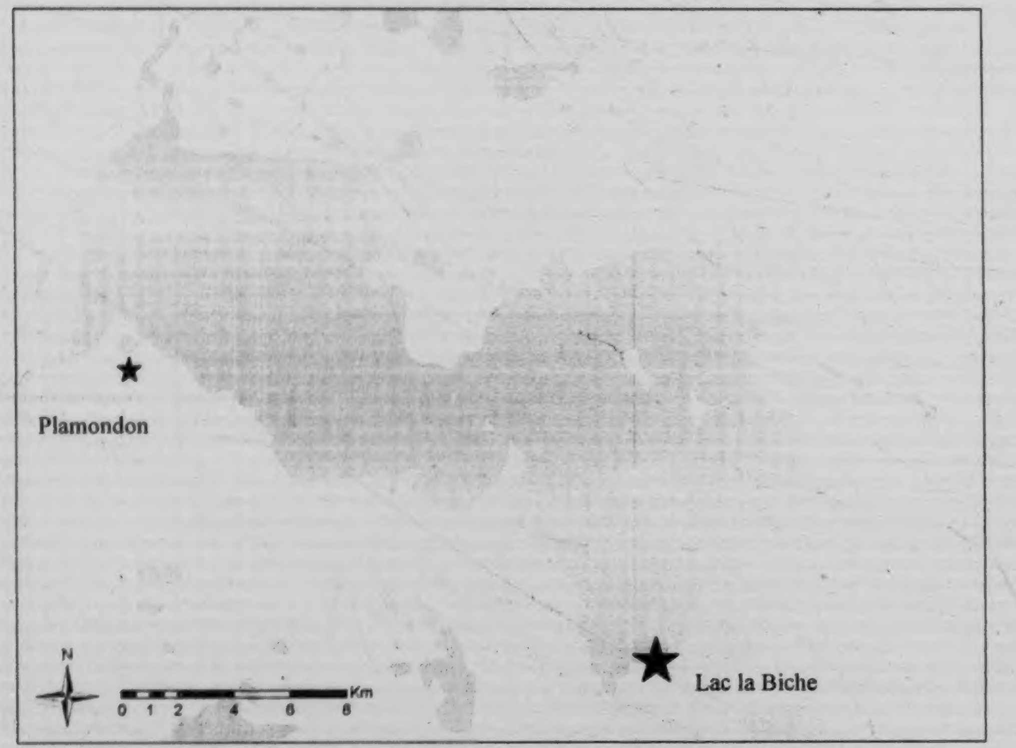


Figure 17: Lac la Biche, Alberta, Canada

Polychlorinated biphenyls (PCBs) were used extensively in North America between the years of 1930 and 1970, as about 37 million kg of Aroclor mixtures were produced in the United States (IARC, 1978) at the peak of their production. The ubiquitous nature of PCB contamination, bioaccumulative properties (Risebrough et al., 1968; Peakall and Lincer, 1970), and adverse environmental (Ratcliff, 1967) and health effects (Fishbein, 1974) led to a ban on industrial PCB production in the mid 1970s. Due to the highly persistent nature of PCBs, in addition to their ability to undergo long-range atmospheric transport (Ballschmiter, 1992), high concentrations are still observed in many ecosystems, including the high Arctic (MacDonald et al., 2000), far from their point of production and usage. The concentrations of these pollutants in these regions have the potential to cause adverse effects of these relatively isolated ecosystems (Muir et al., 1992; Bidleman et al., 1998; Fisk et al., 2005).

Chiral pollutants exist as pairs of non-superimposable mirror images, or enantiomers. Enantiomers of chiral compounds exhibit identical physical and chemical properties, with the exceptions of the direction of rotation of plane-polarized light and their interactions with other chiral molecules. Enantiomers may undergo biochemical interactions with chiral receptors such as enzymes which may interact in a preferential manner with one enantiomer (Williams, 1996). Due to the achiral nature of their synthesis, chiral PCBs are released into the environment as racemates. Because of the identical properties of enantiomers of chiral compounds, physical and chemical processes do not change enantiomeric composition. Because of this, the observation of nonracemic signatures in the environment indicates that the chiral pollutant may be interacting with biological molecules and may be potentially bioprocessed.

Nonracemic EFs are an indication that stereoselective processes are affecting one enantiomer preferentially, or in some cases exclusively. These processes include, but are not limited to species-specific biotransformation at various positions in the food web (Huhnerfuss, 2000), microbial degradation (Huhnerfuss et al., 1993; Benicka et al., 1996; Pakdeesusuk et al., 2003), and biologically- mediated transport across biomembranes, such as the blood brain barrier (Kallenborn et al., 1991).

The objective of this study is to assess the potential occurrence of biomagnification and trophic transfer of PCBs in the LLB food web. The trophodynamics of PCBs in the biota of LLB food web will also be assessed by achiral methods, as discussed in section 1.4.5. This knowledge will be used to assess the potential for human exposure (via diet) to these chemicals. In addition, this project will serve as a starting point for monitoring temporal trends in the food web dynamics of LLB, to be supplemented by future sampling and analysis of chiral PCBs of the aquatic food web.

3.2. Materials and Methods

3.2.1. Sample Collection

Biota samples were taken from May-October 2004. Collection data is presented in Appendix 1. Small fish samples were collected in seine nets, dragged along shallow lake areas. Snails and minnows were collected opportunistically using hand-held nets. Bivalves and benthic invertebrates were collected opportunistically using an Eckmann sampler. Larger fish were collected using variable-mesh gill nets, deployed in deep areas of the lake. Because of the significantly large population of juvenile yellow perch (*Perca flavescens*), efficient collection of northern pike (*Esox lucius*) and walleye was facilitated using rod and reel to avoid collection of large anounts of yellow perch concurrently. Double-crested cormorant (*Phalacrocorax auritus)* specimens were collected opportunistically by shotgun in October of 2004 by Alberta Sustainable Resources and Development. All samples were collected in Whirl-Pak™ (NASCO, Modesto, CA) bags and/or aluminum foil ashed at 400°C for 3h and kept frozen until analysis. Stable isotope analysis (SIA) by isotopic ratio mass spectrometry was conducted on the aquatic food web by Suzanne Earle (Earle, 2006) at the University of Alberta. Approximately 2g of tissue was collected from biota samples for SIA as previously discussed in section 1.4.1.2 to establish trophic structure and organic carbon flow in the LLB food web.

3.2.2. Instrumental Analysis

Samples were extracted according to the procedure described in section 2.2.1. Total PCB and congener analysis was performed using an HP 5980 gas chromatograph equipped with an electron capture detector (ECD). PCBs were separated on a DB-XLB column (30 m × 0.25 i.d. × 0.5 µm df, J&W Scientific). The initial oven temperature of 100°C was ramped to a final temperature of 293°C at a rate of 2.5°C/min in order to facilitate optimal separation of PCB congeners (Frame, 1997). Total PCB concentrations were determined by summing concentrations all analyzed congeners, with the exception of the internal and surrogate standards. Homolog concentrations were determined by summing concentrations of congeners in each homolog group (e.g. $\Sigma_{\text{monochlorinated PCB}}$ = [PCB1]+[PCB2]+[PCB3]). Where samples coelute, concentrations are appropriated in proportion to the number of congeners eluting simultaneously.

3.3. Results

3.3.1. Population Analysis

Yellow perch were observed to be the most abundant fish of the LLB aquatic food web. Yellow perch with a fork length (length between the tip of the snout to the fork of the tail) of less than 5 cm were the most numerous fish in all sampled areas of LLB. Gut content and regurgitate analysis of double-crested cormorants indicate that this size of YLPR constitute approximately 98% of the diet of the cormorant population, with the remainder consisting mainly of two forage fish species: spottail shiner (*Notropis hudsonius*) and brook stickleback (*Culaea inconstans*) (Earle, 2006). This predation pattern has also been observed in the Great Lakes (Diana et al., 2006). Similar observations of double-crested cormorant diet have been made in Lake Ontario, indicating that the cormorant diet consist primarily of yellow perch of about one year of age (Burnett et al., 2002). Due to the high abundance of yellow perch in the food web, it can be concluded that the yellow perch are the most significant prey species in LLB for the cormorant, and other predatory fish in the LLB food web (walleye and northern pike). The high numbers of yellow perch may also suggest that the high cormorant population may also play a role in the regulation of the yellow perch population in LLB by predation (Burnett et al., 2002).

Stable isotope analysis of the aquatic food web of LLB is presented in Figure 19. Of particular note is the relative position of the double-crested cormorant to top predatory fish northern pike and walleye. There is no significant difference in the trophic position of these specimens. This data is in agreement with anecdotal evidence in the local community that suggests that the double crested cormorants are in competetion with top predator fish as a result of overfishing of the walleye population. The $\delta^{15}N$ isotope ratios indicate several distinct trophic levels in LLB fish. There is no significant difference in $\delta^{15}N$ ($p > 0.05$) values between yellow perch, spottail shiner and cisco. Lake whitefish have significantly different $\delta^{15}N$ than the previous group, as well as the top predator fish. When looking at the $\delta^{13}C$ isotopic ratios, it is clear that fish in the LLB food web obtain their diet from similar carbon sources, as there are no significant differences in $\delta^{13}C$ ($p > 0.05$) values between fish. Baseline species analysed for stable isotopes (snail and clam) indicate that forage fish are consuming the same carbon source as snails but not clams.

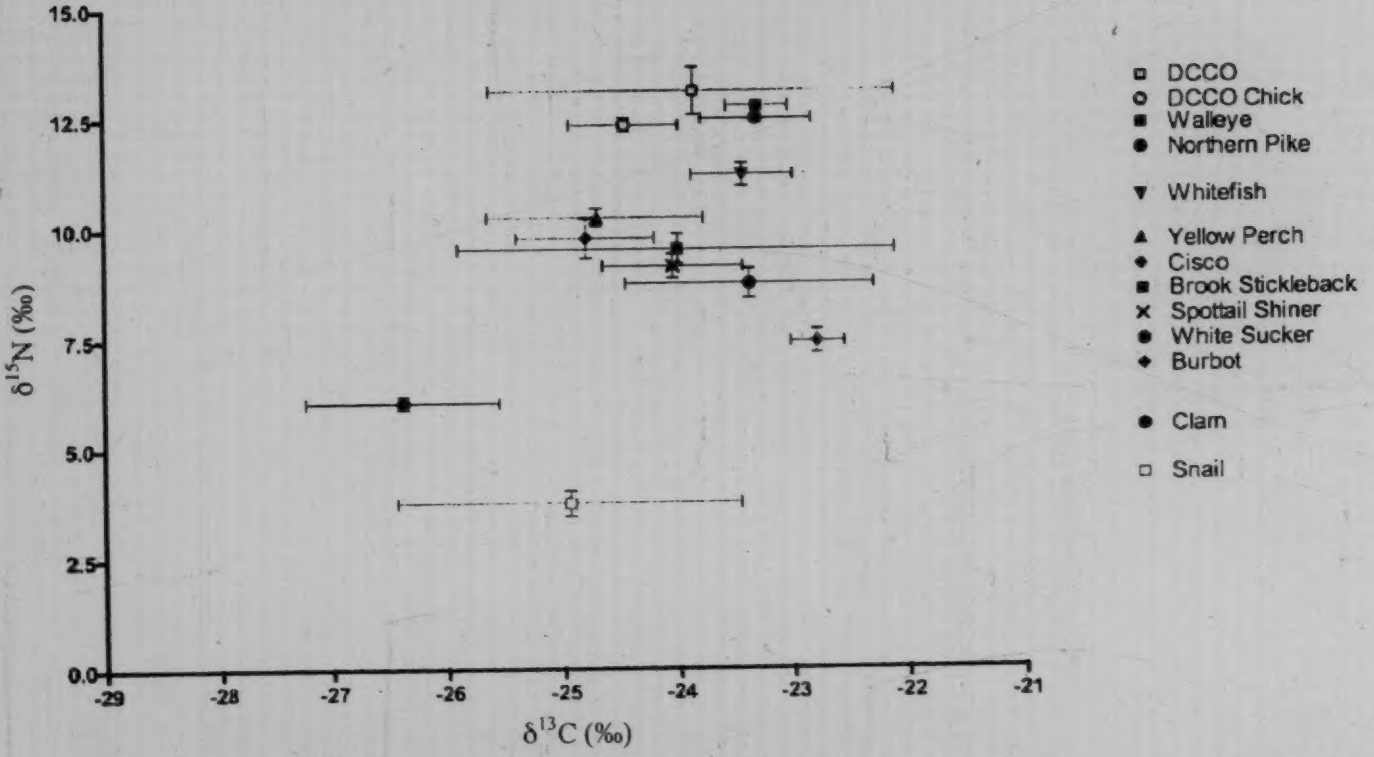


Figure 19: Stable isotope analysis of the LLB food web (Earle, 2006). Error bars represent one standard deviation. Yellow perch sampled are between 5 and 10 cm. in length.

3.3.2. Quality Assurance/Quality Control

Food web data, PCB concentrations, and EFs of chiral PCBs are presented in Tables 8 and 10. Limits of detection were determined by multiplying the standard deviation of baseline by a factor of three (Skoog et al., 1998). Peaks shorter than this amplitude are not detected (ND). Total PCB concentrations of Standard and Certified Reference Material (SRM 1946: Lake Superior Trout tissue, and CRM EC-5, Lake Ontario Sediment) analyzed fell within certified values, and average % recovery of surrogate standards ranged from 77-128% in all cases. Analyte concentrations of SRM/CRM materials used in this study are presented in Chapter 2 (Morrissey et al., 2007), and Wong et al. (2002). Recovery of surrogate standard PCB 204 was significantly higher in double crested cormorant eggs (170%-370%). Concentrations were recovery corrected. Our reported total PCB concentrations in cormorant eggs compare favorably with concentrations previously observed in cormorant eggs from the West coast of Canada (3.8 $\mu g/g_{lipid}$) (Harris et al., 2005), and double-crested cormorant eggs from Lake Michigan (0.38-7.9 $\mu g/g_{lipid}$) (Kannan et al., 2001).

3.3.3. Achiral PCB Analysis

Total PCB analysis is presented in Table 8. Concentrations of individual congeners are listed in Appendix 1. As expected, total PCB concentrations increased in relation to the $\delta^{15}N$ ratio. This was also expected in the cases of PCB 153, a

Table 8: Sampling data for constituents of the Lac La Biche Aquatic Food web (mean ± standard deviation). Values without standard deviations are a result of single samples analyzed or detected. Stable isotope analysis performed by Suzanne Earle (Earle, 2006)

Species	n	% Lipid	$\delta^{13}C$	$\delta^{15}N$	Σ PCB (ng/g_{lipid})	CB153 (ng/g_{lipid})
White Sucker	1	3.749	-23.39 ± 1.08	8.75 ± 0.93	119	1.24
Spottail Shiner	3	1.927 ± 0.821	-24.06 ± 0.61	9.14 ± 1.04	194	3.43
Cisco	4	2.664 ± 1.701	-24.81 ± 0.59	9.76 ± 1.35	388 ± 328	3.20 ± 3.30
Cisco Liver	4	5.468 ± 0.928	NA	NA	594 ± 341	2.44 ± 2.07
Yellow Perch	10	2.805 ± 1.013	-24.72 ± 0.93	10.23 ± 0.98	409 ± 263	5.78 ± 2.26
Yellow Perch Liver	2	4.704 ± 1.089	NA	NA	361 ± 141	4.83 ± 3.87
Lake Whitefish	4	2.175 ± 0.771	-23.45 ± 0.44	11.19 ± 0.51	247 ± 96.0	4.64 ± 1.78
Lake Whitefish Liver	2	9.283 ± 7.598	NA	NA	286 ± 252	3.70 ± 3.30
Northern Pike	16	2.578 ± 0.199	-23.33 ± 0.48	12.46 ± 0.19	837 ± 455	14.2 ± 12.2
Northern Pike Liver	7	8.340 ± 2.041	NA	NA	669 ± 599	21.0 ± 19.9
Walleye	2	1.013 ± 0.248	-23.32 ± 0.27	12.75 ± 0.21	932 ± 250	13.2 ± 5.32
Walleye Liver	2	6.371 ± 2.257	NA	NA	729 ± 737	22.7 ± 22.8
DCCO Chick	3	2.141 ± 0.271	-24.48 ± 0.47	12.32 ± 0.64	2220 ± 243	89.5 ± 5.13
DCCO Chick Liver	4	3.470 ± 1.187	NA	NA	2120 ± 874	79.7 ± 24.0
DCCO Egg	3	4.627 ± 0.732	-24.30 ± 1.08	12.66 ± 0.73	2040 ± 501	132 ± 24.4
DCCO	4	6.268 ± 1.561	-24.30 ± 1.08	12.66 ± 0.73	4040 ± 2230	341 ± 278
DCCO Liver	4	4.594 ± 1.113	NA	NA	3650 ± 1870	204 ± 123

recalcitrant congener, as well as the more highly chlorinated congeners. In all species, total concentration of PCBs increased relative to that of a recalcitrant congener, in this case, PCB 153 (r^2=0.126-0.946, $p<0.05$). Statistical outputs are presented in Appendix 2. This is indicative of bioconcentration of total PCB burden. There was no significant increase in total CB concentration with PCB 153 in the case of DCCO chicks (r^2=0.0253, p=0.898). One possible reason for this difference may be is due to the limited metabolic capability of DCCO chicks, which have a lower capacity for biotransformation because of their lower energy requirements compared to those of adult birds (Gabrielsen et al., 1991; Konarzewski et al., 1993; Klaassen, 1994; Weathers and Siegel, 1995). Another possibility is that concentrations have not become high enough to induce bioprocessing by CYP enzymes (Safe et al., 1985; Tillitt et al., 1992; Boon et al., 1997). Biomagnification of total PCBs and PCB 153 was also observed in the biota of LLB (Figures 20, 21). These results may be skewed by the inclusion of DCCO as a part of the LLB biota, as lipid normalized concentrations for total PCBs are significantly different from those of top predator fish (p=0.048). Higher total PCB concentrations in DCCO may be as a result of contamination from more highly contaminated fish from lower latitudes, as DCCO are a migratory species. These concentration patterns have been observed in double-crested cormorants feeding in highly contaminated regions of the Southern California Bight (Glaser and Connolly, 2002).

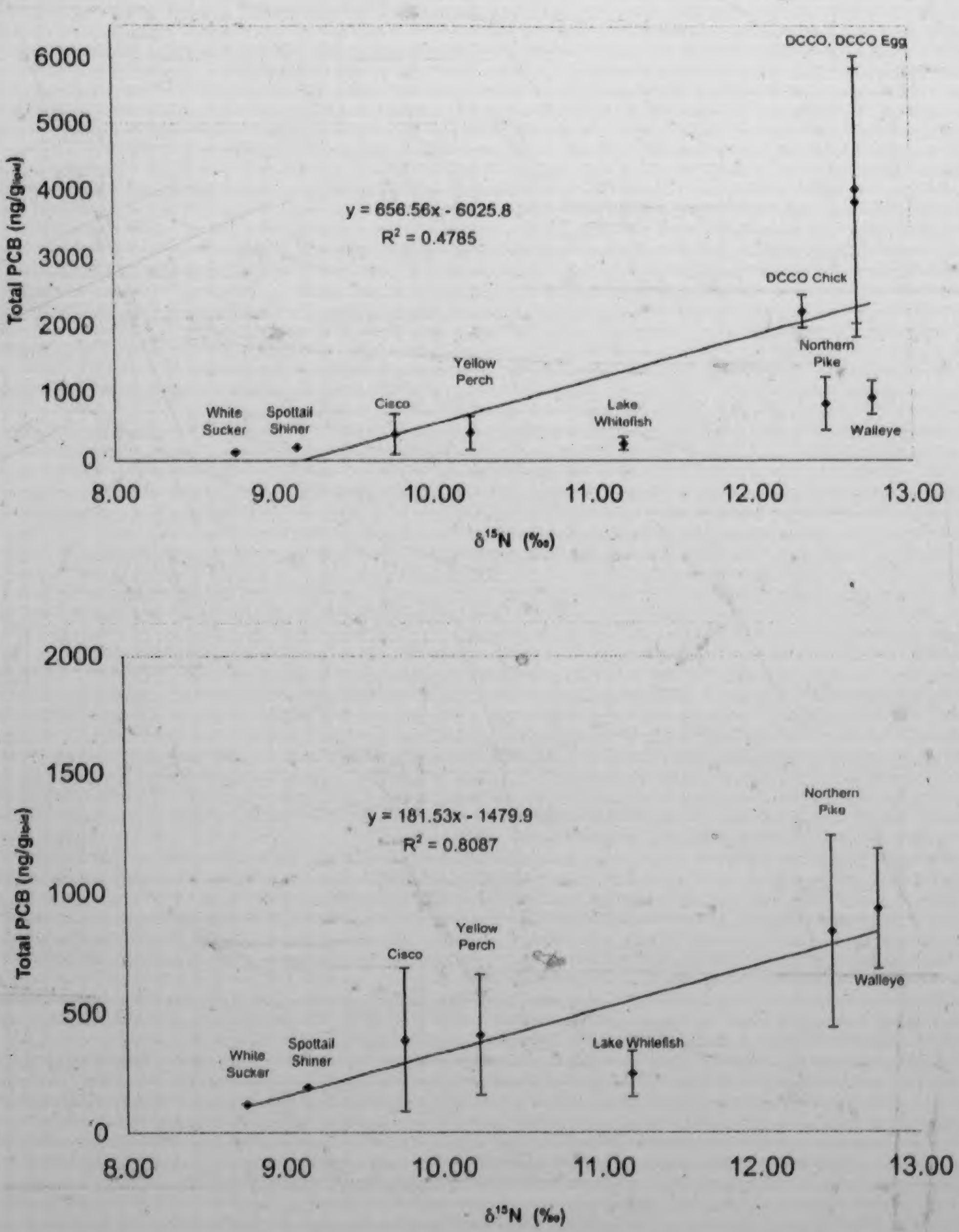


Figure 19: Biomagnification of Total PCBs in the LLB aquatic food web ($p<0.05$ for both cases)

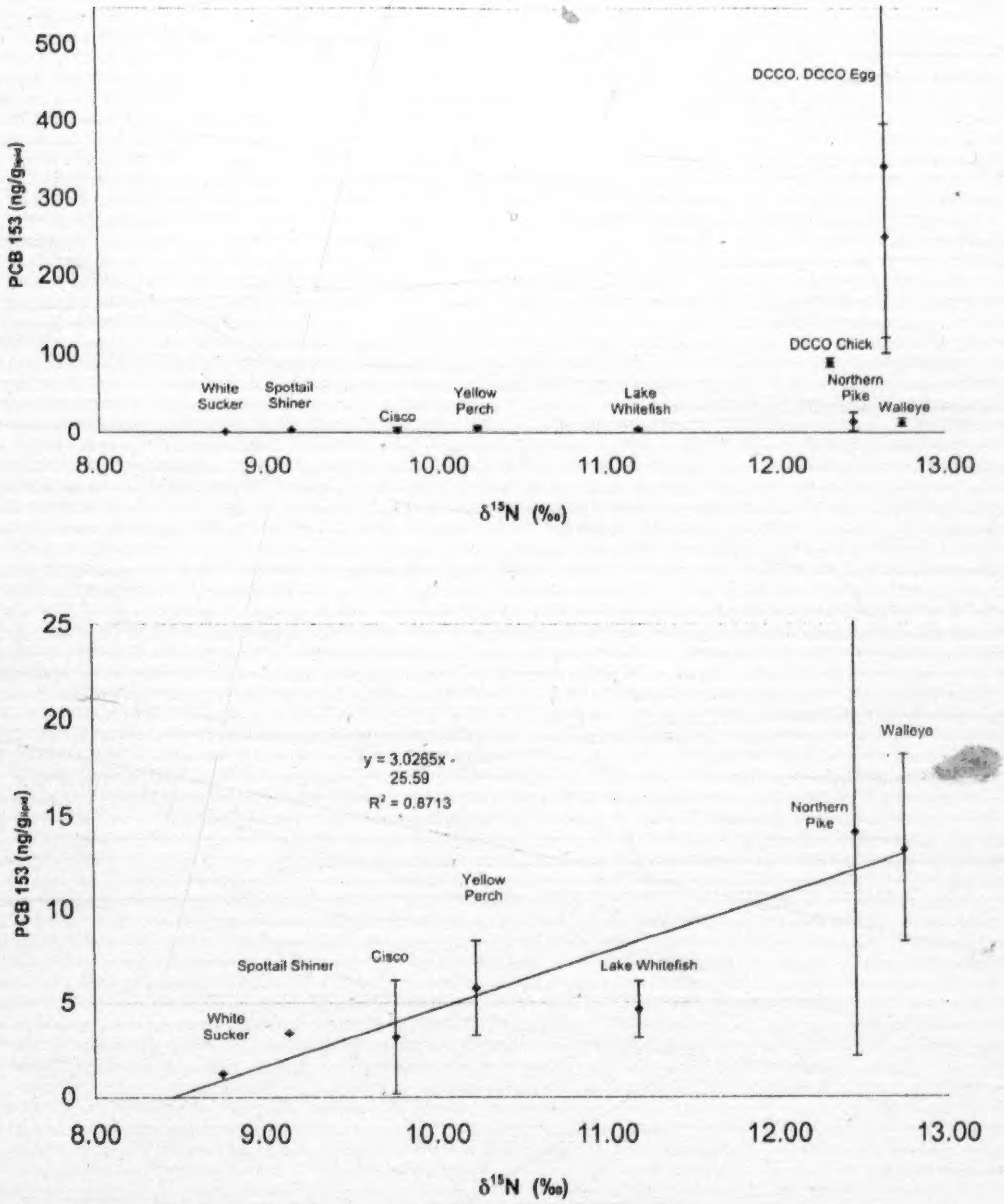


Figure 20 : Biomagnification of PCB 153 in the LLB aquatic food web ($p<0.05$ in both cases)

Chiral PCB congener concentrations were not statistically significant between samples in different lake basins of LLB for northern pike (p>0.3 among basins). Sample sizes for other fish species were too small to determine statistical differences between basins. This is indicative that the source of PCB contamination in LLB is as a result of long range atmospheric transport throughout the LLB watershed, and not as a result of point-sources of PCB contamination. This hypothesis is further reinforced by observations of PCB concentrations in Lake Winnipeg, with concentrations in LLB on the same order of magnitude for biota in the North basin of Lake Winnipeg of similar trophic level. Biota in the North Basin of Lake Winnipeg also had significantly different concentrations than the South Basin (Rawn et al., 2000; Gewurtz et al., 2006). This is supported by the limited mixing events occurring in LLB, and poor circulation of water between basins. This may also be an indicator of point-source contamination being equal throughout the three basins from the town of LLB (Town basin), the town of Plamondon (West basin) and the cottage villages surrounding the shores of the East basin of LLB.

Congener profiles are illustrated in Figures 22 and 23. PCB congener profiles for LLB fish are similar, and the congener profile pattern for DCCO tissue, liver and eggs indicates a greater capacity for the biotransformation of lower chlorinated congeners (Kannan et al., 2001). Other PCB congeners with vicinal meta-para hydrogen atoms are observed to be in lower proportions in double crested cormorants, indicating that avians have higher metabolic capacity than fish to biotransfrom PCBs (Buckman et al., 2004; Warner et al., 2005). The observed congener ratios are consistent with observations that CYP mediated processes likely dominated biotransformation of PCBs in higher trophic level organisms (Buckman et al., 2006). Congener profiles also appear to differ between liver tissues and axial muscle tissue. This may be indicative of biotransformation of low-chlorinated congeners in the livers of northern pike and walleye, which would skew the congener profile in this manner (Borga et al., 2004; Buckman et al., 2004; Wong et al., 2004).

One means to determine the potential occurrence of biotransformation of PCBs via achiral analysis is to determine the relative concentration change of a congener of interest normalized to a concentration of a recalcitrant congener for predator and prey. This is illustrated in Figure 24 for chiral PCB congeners 91, 95, 136, and 149. In general, values of this fraction greater than 1 indicate bioaccumulation, whereas values lower than one indicates potential biotransformation of the congener from prey to predator (Stegeman and Kloepper-Sams, 1987; Boon et al., 1989). It was observed that double-crested cormorants have the ability to biotransform chiral PCB congeners 95 and 149. PCBs 91 and 136 were not detected in DCCO tissue, indicating that DCCO have the ability to biotransform these congeners to below detectable concentrations.

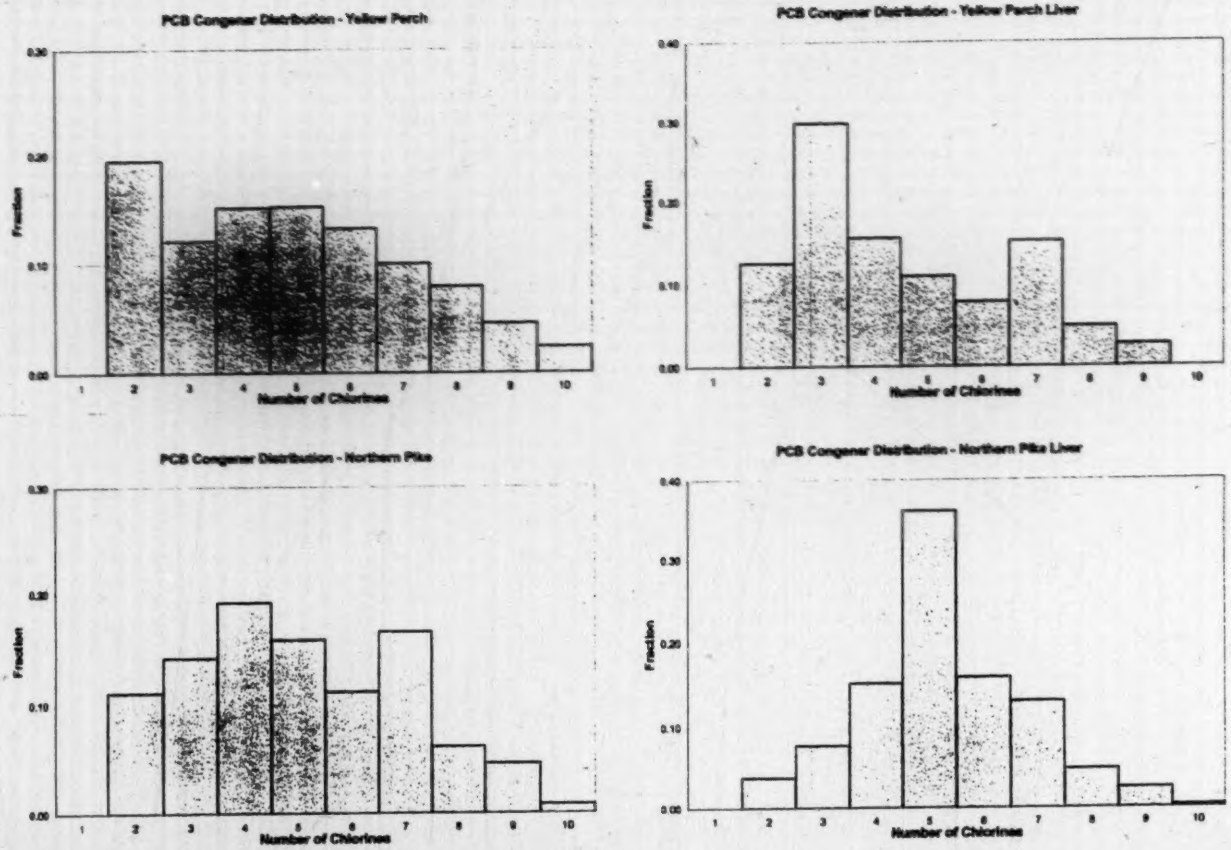


Figure 22: Total PCB congener profiles for selected fish in the LLB food web. Plots indicate average homolog concentrations for each species. Sample sizes are given in Table 8 (p. 87).

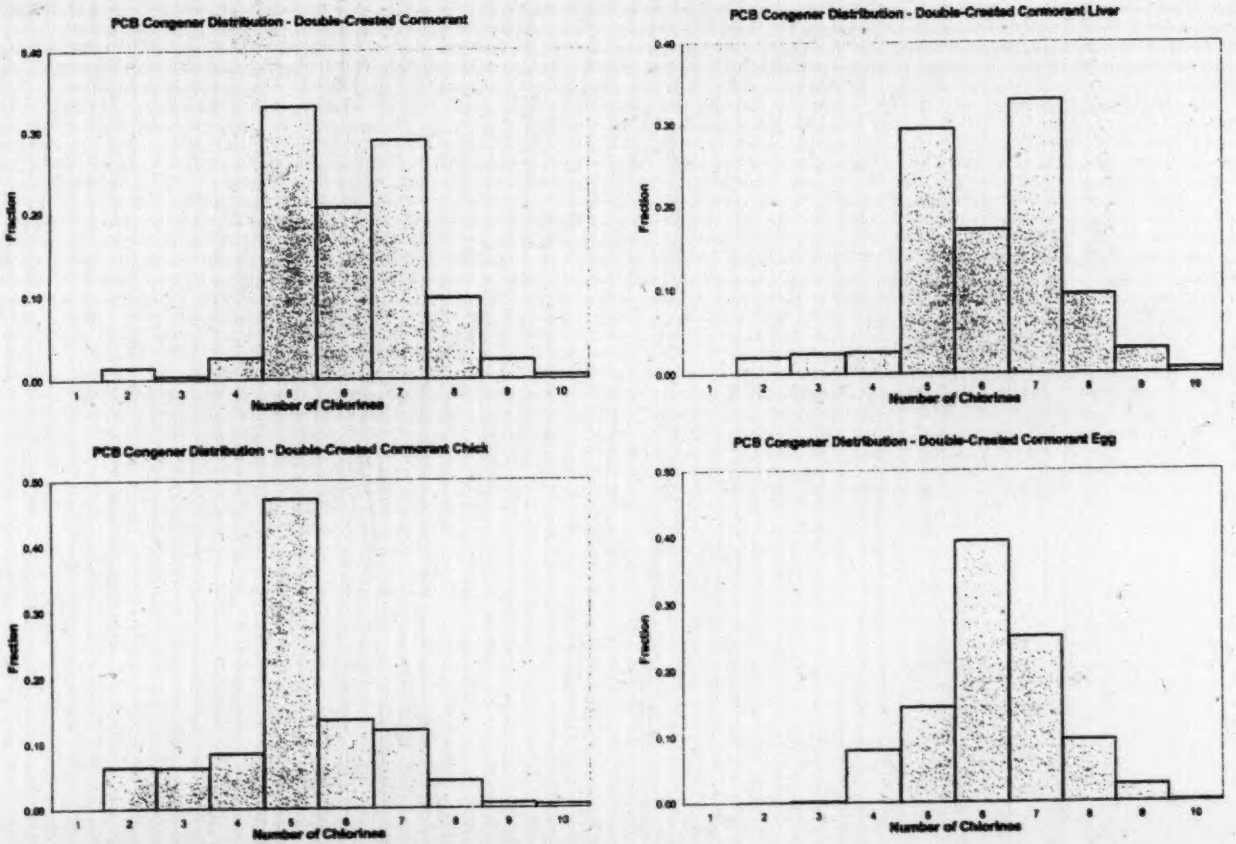


Figure 23: PCB Congener distribution in the double-crested cormorant tissues. Plots indicate average homolog concentrations for each sample type. Sample sizes are given in Table 8 (p. 87).

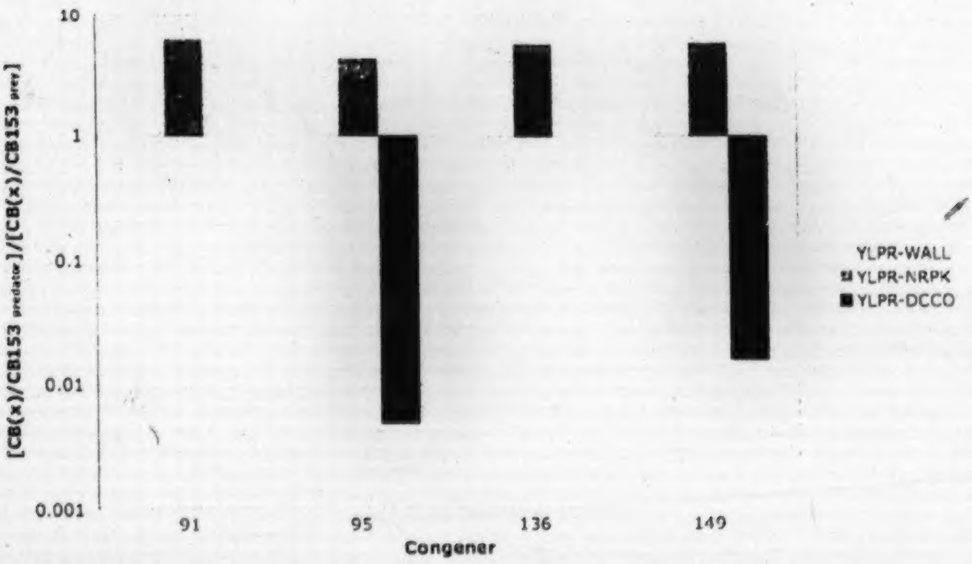


Figure 23: Relative concentration ratios of chiral PCB congeners in Lac La Biche top predators.

There are several problems with using this method. Foremost, it is not known whether the change in concentrations of the chiral congeners is due to biotransformation, or incomplete absorption of these congeners form the diet. Furthermore, this calculation assumes that the predator is consuming only one type of prey, which is not realistic. Although yellow perch are abundant, they are not the only source of food for predators of LLB (Earle, 2006). The relative ratio method also does not actively measure the occurrence of biotransformation at rates lower than rates of uptake (Wong et al., 2004). While concentrations may increase, biotransformation may also occur, however, using achiral analysis, this information remains unknown. Similar comments may be made concerning biomagnification factors (See Section 1.4.4) (Table 9). In almost every case, PCB congeners gave a

BMF greater than unity. However biotransformation may still be occurring (Wong et al., 2002), which may be confirmed by chiral analysis.

Table 8: Biomagnification factors of PCB congeners in the aquatic food web of Lac La Biche

	Biomagnification Factor (BMF)				
Congener	**Whitefish-Perch**	**Whitefish-Spottail**	**Pike-Perch**	**Pike-Spottail**	**Pike-Whitefish**
45	NA	1.14	NA	2.26	1.98
91	NA	0.77	NA	1.91	2.49
95	1.58	0.97	2.95	1.82	1.87
136	3.21	NA	2.47	NA	0.77
149	2.63	2.67	3.50	3.54	1.33
PCB 153	0.80	1.08	2.45	6.13	5.68
Σ PCB	0.60	1.48	2.05	3.45	2.34

3.3.4. Chiral PCB Analysis

Concentrations of chiral PCB congeners are presented in Table 10. Chiral PCB congeners 45, 91, 136, 174, and 183 were not detected in several samples of the lower trophic levels of LLB. EF data presented are results observed from detectable samples (Figures 25-30). In general PCBs 149 and 95 were present in the highest concentrations, PCBs 45, 191, 136, and 183 were not detected in several constituents of the LLB food web, and were primarily detected at higher trophic levels. PCB 174 was only observed in one DCCO egg sample as well as two northern pike liver samples and one northern pike fish tissue samples. In northern pike, PCB 174 enantiomers were observed in racemic proportions, whereas in DCCO, depletion of the (-)-enantiomer was observed.

Enantiomeric fractions of chiral PCBs in the biota of LLB are reported in Figures 2-7. PCB 45 was not detected in double-crested cormorant adult pectoral muscle tissue, and only in low concentrations in cormorant liver tissue. It was easily detected in cormorant eggs however, indicating that the cormorant has a high metabolic capacity for this congener, as the presence of it in egg samples is a "snapshot" of the PCB burden of the adult. This is reinforced by the congener profile of cormorant (Figure 23) illustrating a lower fraction of low chlorinated PCBs. Racemic EFs of PCB 45 were detected in lake whitefish, northern pike, and walleye in both muscle tissue and liver samples. EFs on PCB 45 were also racemic in samples from double-crested cormorant chicks and adults at concentrations less than 2 ng/g_{lipid}. Nonracemic EFs of PCB 45 were observed in DCCO egg samples (EF=0.401 ± 0.032).

	Congener concentration (ng/g $_{lipid}$)						
Species	**45**	**91**	**95**	**136**	**149**	**174**	**183**
White Sucker	ND	0.02	0.14	0.03	0.26	ND	0.16
Spottail Shiner	0.61	0.28	0.68	ND	0.97	ND	ND
Cisco	ND	0.60 ± 0.07	4.98 ± 3.19	0.10 ± 0.09	4.37 ± 3.62	ND	ND
Cisco Liver	ND	0.42	6.15 ± 7.14	ND	3.51 ± 3.53	ND	1.05
Yellow Perch	ND	0.14 ± 0.07	0.42 ± 0.11	0.03 ± 0.01	0.97 ± 0.24	ND	ND
Yellow Perch Liver	ND	3.90 ± 0.07	3.17	1.99	6.14 ± 5.10	ND	ND
Lake Whitefish	0.7	0.22 ± 0.07	0.67 ± 0.38	0.09 ± 0.05	2.57 ± 1.06	ND	ND
Lake Whitefish Liver	0.17 ± 0.18	0.07 ± 0.07	0.31 ± 0.03	0.02 ± 0.01	0.72 ± 0.40	ND	ND
Northern Pike	13.4 ± 15.2	3.18 ± 0.07	6.14 ± 7.55	0.56 ± 0.47	19.3 ± 19.3	0.58	3.76 ± 4.06
Northern Pike Liver	1.38 ± 1.39	0.54 ± 0.07	1.25 ± 0.57	0.07 ± 0.05	3.42 ± 2.28	0.94 ± 1.21	3.17 ± 2.52
Walleye	3.94	4.21 ± 0.07	10.4	ND	17.9 ± 11.1	ND	7.17
Walleye Liver	0.30	0.08 ± 0.07	5.78 ± 5.13	0.05 ± 0.01	3.95 ± 3.23	ND	ND
DCCO Chick	2.12	ND	0.77	ND	1.72	ND	9.72 ± 8.21
DCCO Chick Liver	ND	ND	0.13 ± 0.08	ND	1.94 ± 1.44	ND	4.88 ± 4.29
DCCO Egg	0.03 ± 0.01	ND	0.03 ± 0.03	ND	0.11 ± 0.04	0.147	34.3 ± 13.0
DCCO	ND	ND	0.12 ± 0.05	ND	0.92 ± 0.51	ND	61.6 ± 61.1
DCCO Liver	0.16 ± 0.01	ND	0.16 ± 0.08	ND	1.42 ± 1.44	ND	42.7 ± 34.9

Table 10: Concentrations of target chiral PCB atropisomers (mean± standard deviation) in the Lac La Biche aquatic food web. (ND=not detected)

Racemic EFs of PCBs 91 and 95 were observed throughout smaller fish sampled (yellow perch, and spottail shiner). In cisco and whitefish, racemic EFs of both PCB 91 and 95 were observed in muscle tissue, however nonracemic PCB 91 was observed in the liver tissue of cisco (EF=0.422), (EF=0.368), and white sucker (EF=0.412). However, the observed peaks for the enantiomers of PCB 91 in these samples were near the limit of detection (LOD), and below the limit of quantification (LOQ). For the purposes of this study, the LOD is defined as being three times the standard deviation of baseline signal, whereas the LOQ is 10 times the standard deviation of baseline signal. Because of this, it is difficult to conclude whether these EFs are significantly nonracemic. There were no statistically significant differences between EFs of all LLB food web constituents studied. Nonracemic EFs of PCB 95 were also observed in whitefish liver (avg. EF = 0.435). For predatory fish, racemic EFs of PCB 95 were observed in both walleye and northern pike for both tissue and liver samples. PCB 91 was nonracemic in northern pike liver (EF=0.396 ± 0.051) but not walleye liver (EF=0.524). PCB 91 was not detected in DCCO chick muscle, chick liver, adult muscle, adult liver, or eggs using chiral GC/MS. Racemic EFs of PCB 95 were detected in cormorant chick and adult breast tissue, as well as chick liver samples. Nonracemic EFs of PCB 95 were observed in adult cormorant livers, and in egg samples, both indicating depletion of the first eluting enantiomer.

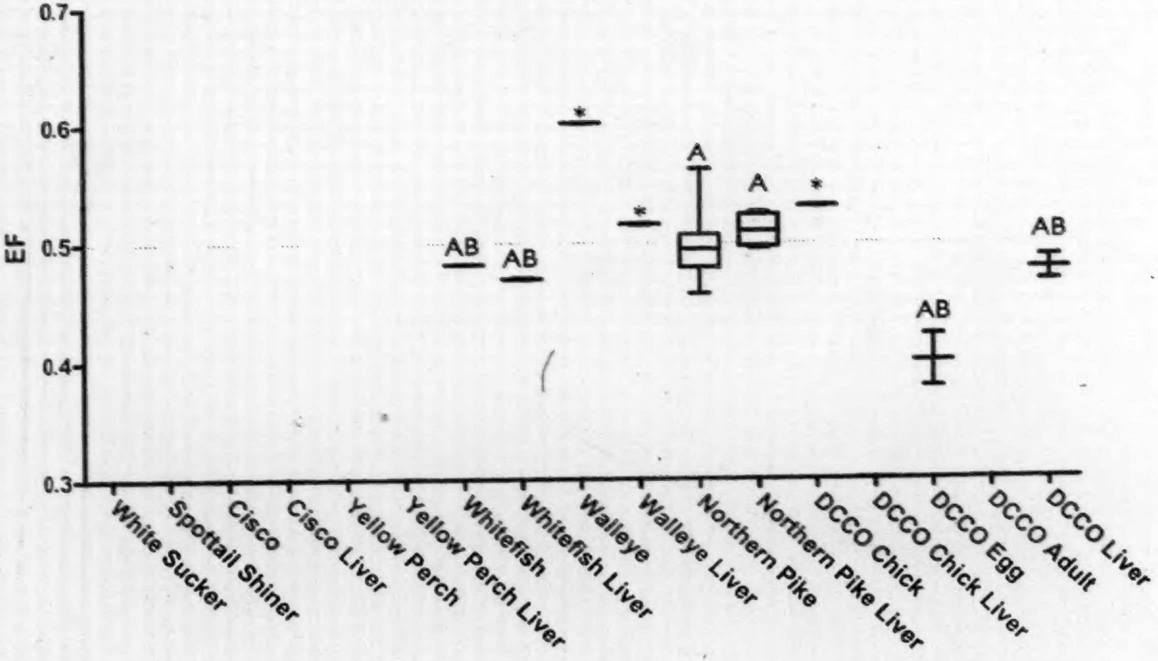


Figure 25: Enantiomer Fractions of PCB 45 in the Lac La Biche aquatic food web. PCB 45 was not detected in white sucker, spottail shiner, cisco, yellow perch, cormorant chick liver and cormorant adults. Dotted Line at EF=0.5 indicates racemic EF. Edges of boxes indicate 25th and 75th percentile. Box edges represent maximum and minimum values. Horizontal line in box represents median value. Differing letters above data indicate significant differences between sample groups. Points indicated with an asterisk were not included in Tukey's multiple comparison test due to low sample detection rates (n>2).

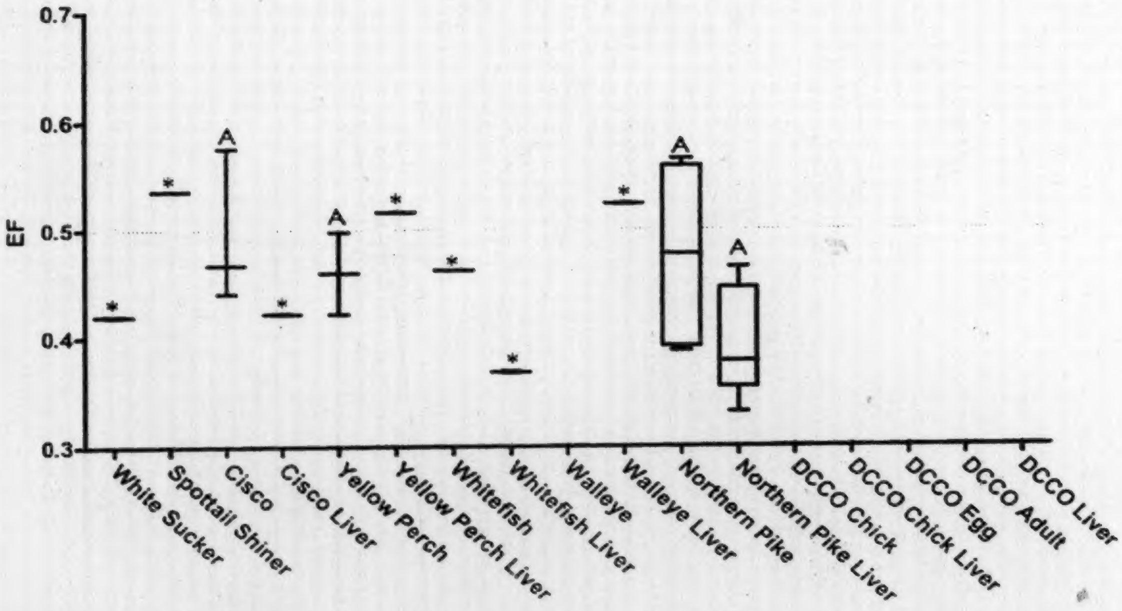


Figure 26: Enantiomer Fractions of PCB 91 in the Lac La Biche aquatic food web. PCB 91 was not detected in walleye and all types of cormorant tissue studied. Dotted line at EF=0.5 indicates racemic EF. Edges of boxes indicate 25th and 75th percentile. Box edges represent maximum and minimum values. Horizontal line in box represents median value. Differing letters above data indicate significant differences between sample groups. Points indicated with an asterisk were not included in Tukey's multiple comparison test due to low sample detection rates (n>2).

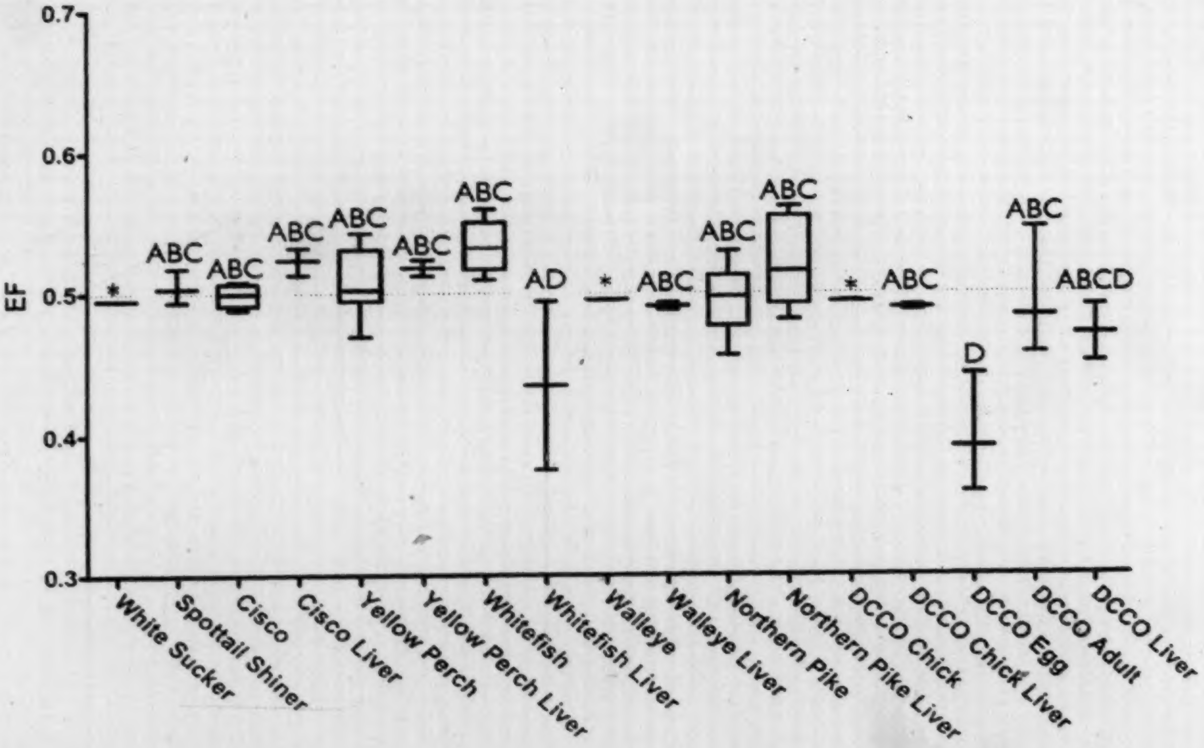


Figure 27: Enantiomer Fractions of PCB 95 in the Lac La Biche aquatic food web. Dotted line at EF=0.5 indicates racemic EF. Edges of boxes indicate 25th and 75th percentile. Box edges represent maximum and minimum values. Horizontal line in box represents median value. Differing letters above data indicate significant differences between sample groups. Points indicated with an asterisk were not included in Tukey's multiple comparison test due to low sample detection rates (n>2).

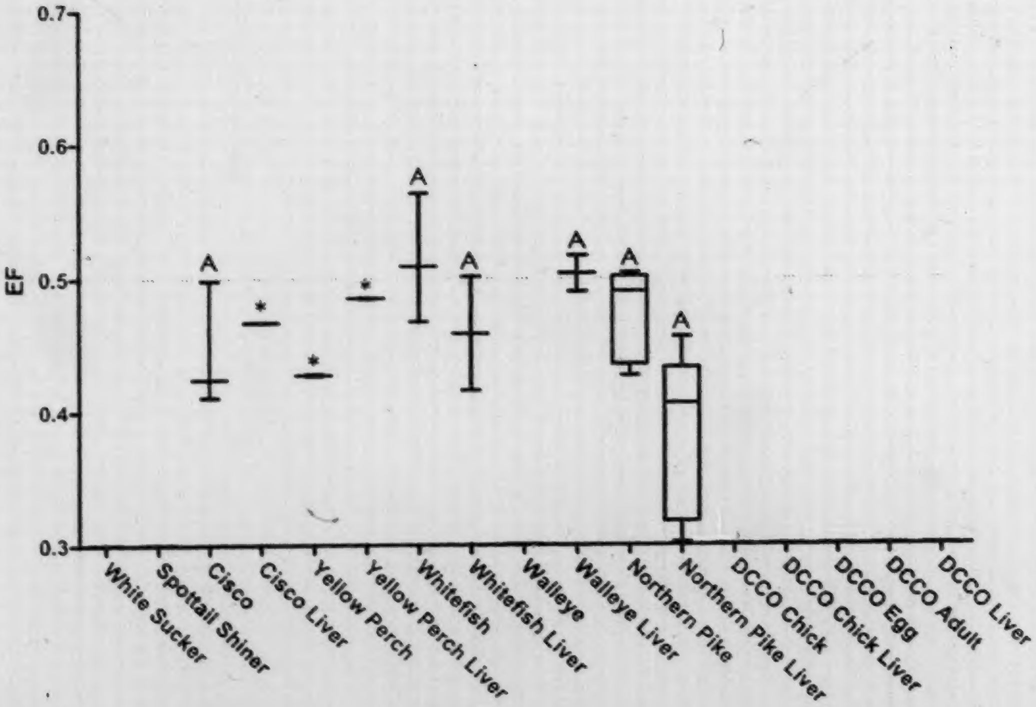


Figure 28: Enantiomer Fractions of PCB 136 in the Lac La Biche aquatic food web. PCB 136 was not detected in white sucker, spottatil shiner, walleye and all types of cormorant tissue studied. Dotted line at EF=0.5 indicates racemic EF. Edges of boxes indicate 25th and 75th percentile. Box edges represent maximum and minimum values. Horizontal line in box represents median value. Differing letters above data indicate significant differences between sample groups. Points indicated with an asterisk were not included in Tukey's multiple comparison test due to low sample detection rates (n>2).

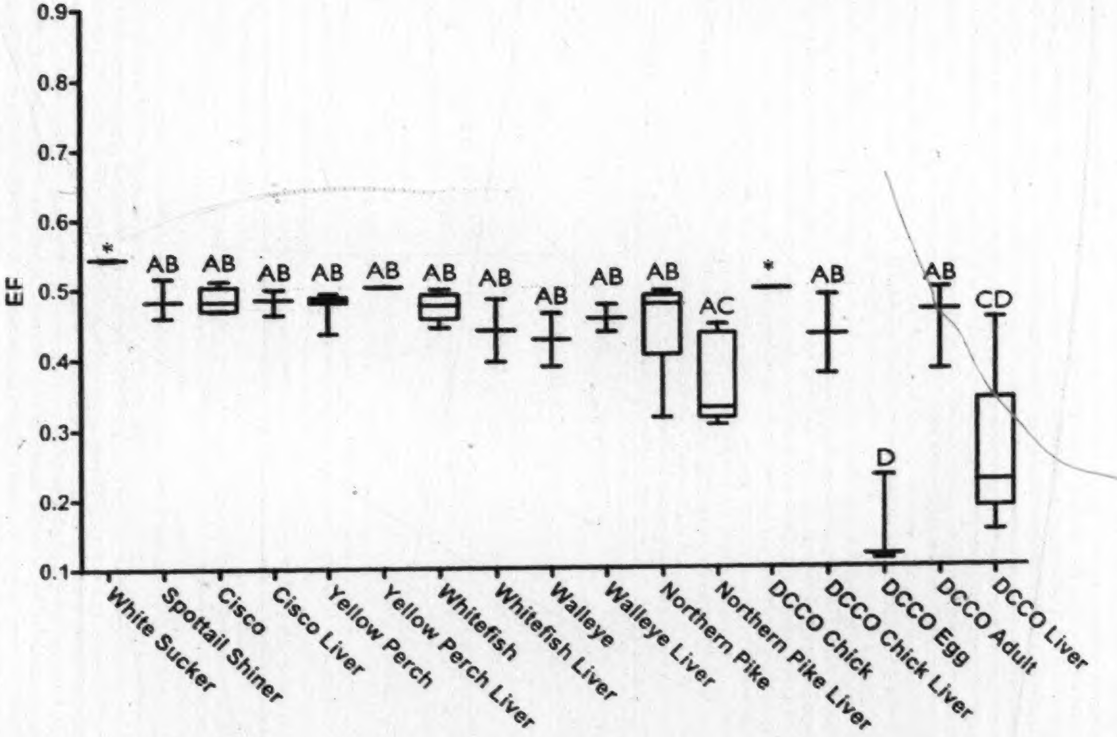


Figure 29: Enantiomer Fractions of PCB 149 in the Lac La Biche aquatic food web. Dotted line at EF=0.5 indicates racemic EF. Edges of boxes indicate 25th and 75th percentile. Box edges represent maximum and minimum values. Horizontal line in box represents median value. Differing letters above data indicate significant differences between sample groups. Points indicated with an asterisk were not included in Tukey's multiple comparison test due to low sample detection rates (n>2).

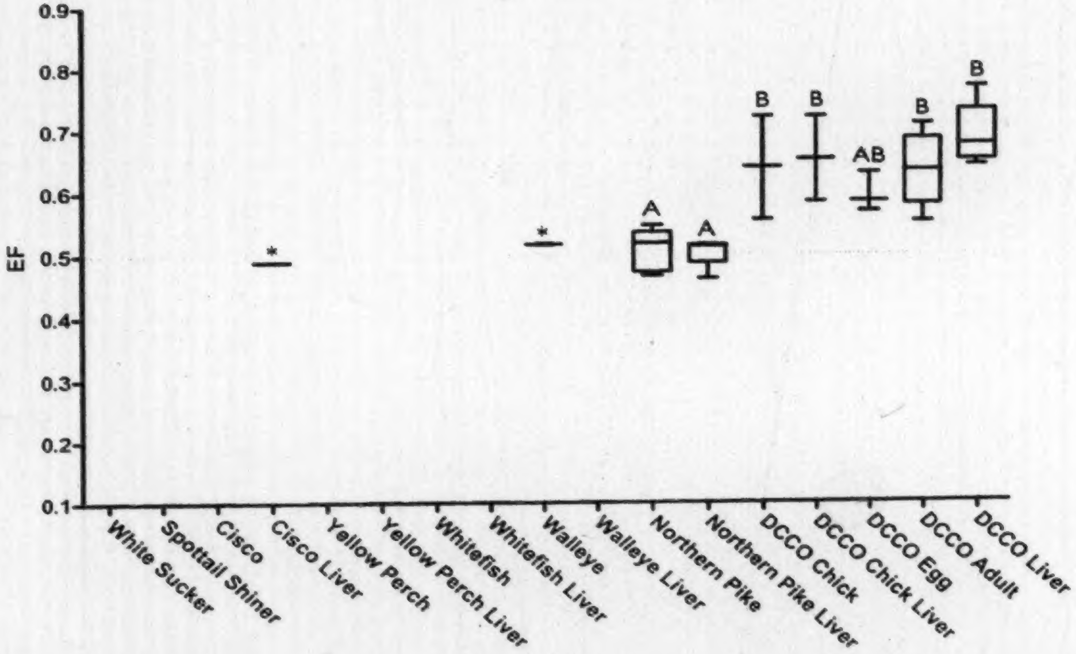


Figure 30: Enantiomer Fractions of PCB 183 in the Lac La Biche aquatic food web. PCB 183 was not detected in fish samples, except cisco liver, walleye filet, and northern pike filet and liver tissues. Dotted line at EF=0.5 indicates racemic EF. Edges of boxes indicate 25th and 75th percentile. Box edges represent maximum and minimum values. Horizontal line in box represents median value. Differing letters above data indicate significant differences between sample groups. Points indicated with an asterisk were not included in Tukey's multiple comparison test due to low sample detection rates (n>2).

Nonracemic EFs of PCB 136 were detected in whole yellow perch (EF=0.375 ± 0.075), cisco filet tissue (EFs=0.444 ± 0.047), whitefish liver (EF=0.459), and northern pike liver (EFs= 0.381 ± 0.063). Racemic EFs were observed in both whitefish and northern pike filet tissues. All nonracemic EFs observed in the LLB food web had an EF of less than 0.5, indicating that there was significant depletion of the (-)-enantiomer with respect to the (+)-enantiomer.

Racemic EFs of PCB 149 were detected in the lower food web (spottail shiner, cisco, yellow perch, lake whitefish), while nonracemic EFs were observed in walleye and northern pike, the top predator fish species (average EFs=0.425 and 0.446, respectively). Northern pike and walleye liver samples also exhibited nonracemic rations of PCB 149 (average EFs= 0.366 and 0.456, respectively). Statistically nonracemic EFs on PCB 149 were observed in all adult cormorant breast tissue, liver tissue, eggs, and chick liver tissue (average EFs = 0.447, 0.263, 0.179. and 0.373, respectively). Racemic PCB 149 was observed in cormorant chick muscle tissue (average EF = 0.4970). As was the case with PCB 136, all nonracemic EFs indicated depletion of the (-)-enantiomer with respect to the (+)-enantiomer.

All fish samples exhibited racemic EFs for PCB 183. Average EFs of PCB 183 in the fish samples ranged from 0.489 in cisco liver tissue to 0.509 in northern pike filet tissue. The (-)-enantiomer of PCB 183 was significantly depleted in all double-crested cormorant samples, in both chick and adult muscle tissue (average EF=0.638 and 0.632) and liver tissue samples (average EF=0.652 and 0.690, respectively). Nonracemic PCB 183 was also observed in the eggs of the double-crested cormorant (EF=0.592).

Significantly nonracemic EFs of PCBs were observed in whitefish, northern pike, and walleye. In northern pike filet tissue, racemic EFs of chiral PCBs 45, 91, 95, 136, 174, and 183 were observed, however the concentration of PCB 149 was significantly different from racemic PCB 149 (EF= 0.446). Statistically nonracemic EFs of chiral PCB congeners 91 (EF=0.396 ± 0.051), 136 (EF=0.381 ± 0.063), 149(EF=0.366 ± 0.064) were observed in northern pike liver samples. Lipid-normalized concentrations of PCB 45 were observed to be lower in double crested cormorant samples than in their diet. This indicates a higher capacity for DCCO to biotransform PCBs that exhibit a low degree of chlorination.

There was a weak but not statistically significant correlation between total PCB concentration and EFs of PCB 95 (p=0.933) (Figure 31) and PCB 149 (p=0.505) (Figure 32) in northern pike. Correlations were stronger for relationships of PCB 153 concentrations and EFs of PCB 95 (r^2=0.2591) and PCB 149 (r^2=0.1746), however these relationships were also not statistically significant (p=0.065 and 0.121, respectively). EF-size relationships were all not statistically significant for northern pike liver concentrations. In the case of PCB 95, this may suggest that the degree of enantioselective biotransformation may be related to concentration of PCB 153. There was also no significant observed relationship between EF of PCB 95 (p=0.487) and PCB 149 (p=0.184) and fish size, as measured by fork length in northern pike (Figure 33), although the EFs were better correlated with fork length for PCB 149 (r^2=0.131) than for PCB 95 (r^2=0.041). There were no statistically significant correlations between congener concentration and EFs of northern pike for all chiral PCB congeners. This indicates that the stereoselective biotransformation of chiral PCBs may not be concentration dependent in the LLB food web.

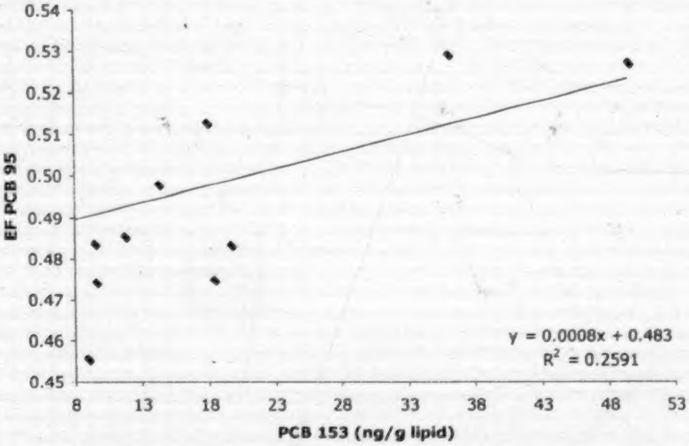


Figure 30: Lipid normalized PCB 153 concentrations vs. EFs of PCB 95 in Northern Pike (p=0.06).

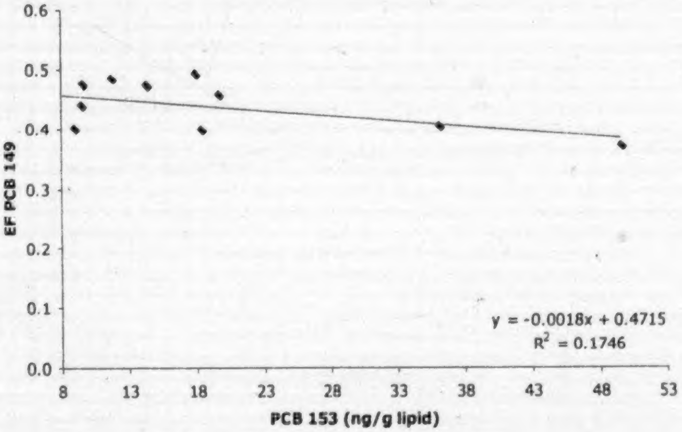


Figure 31: Lipid normalized PCB 153 concentrations vs. EFs of PCB 149 in Northern Pike (p=0.141).

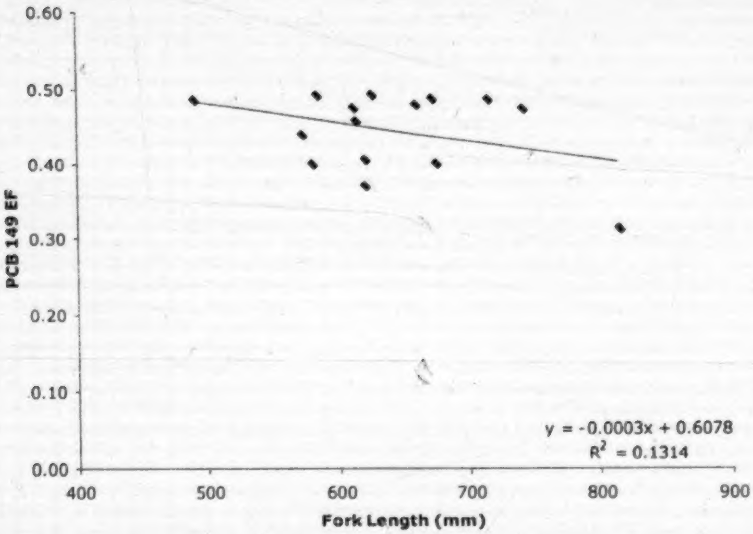


Figure 32: Variation in EF with fork length in northern pike of LLB (p=0.184)

3.4. Discussion

3.4.1. Chiral PCBs in Forage Fish

All EFs of each forage fish species were also not statistically different from racemic based on our observations. This data suggests that enantioselective biotransformation is not occurring in these species (Vetter et al., 2001; Wong et al., 2002; Wong et al., 2004; Warner et al., 2005). Previous food web studies have shown that enantioselective elimination of PCBs 95, 174, and 183 may be occurring in slimy sculpin in Lake Ontario (Wong et al. 2004), as significant depletion of the first eluting enantiomer was observed for PCB 95, and depletion of the (+)-enantiomer was observed for PCBs 174 and 183. In the same study, depletion of the first eluting enantiomer of PCB 91 was observed in cisco, all other EFs of chiral PCB congeners were observed to be racemic. Our results for forage fish are similar in cisco and whitefish. While the EF for PCB 91 in cisco is not significantly racemic, the same enantiomer is enriched, indicating that depletion of the first eluting enantiomer may be occurring. Significantly nonracemic EFs of PCB 91 are observed in whitefish in LLB. This may as a result of its higher trophic position in comparison to cisco. The EFs of yellow perch, like the cisco, did not indicate the potential for enantioselective biotransformation of chiral PCBs. There have been no previous studies on the enantiomer composition of PCBs in the yellow perch.

Stereoselective biotransformation of chiral PCB congeners has been previously observed in constituents at this trophic level. Warner et al. (2005) observed racemic EFs in forage fish of the Northwater Polynya. Nonracemic PCBs have also been observed in freshwater sculpins (Wong et al., 2001), as well as reports of chiral methylsulfonyl PCB metabolites in sculpin species (Stapleton et al., 2001), which indicate the occurrence of biotransformation of PCBs. Stereoselective elimination of chiral PCBs has also been confirmed in plankton species, based on observations in field measurements of EFs of chiral PCBs in arctic marine zooplankton (Borga and Bidleman, 2005), and the freshwater invertebrates *Diporeia* and *Mysis relicta* (Wong et al., 2004).

3.4.2. Chiral PCBs in Top Predator Fish

Low numbers of walleye samples are because walleye are rare in LLB, due to overfishing. Restocking efforts have largely failed in LLB. Models suggest that areas with a high cormorant population require population control in order to re-stock lakes with a sustainable walleye population, in order to prevent predation by the cormorant population on the re-stocked walleye fingerlings (Duffy, 1995; Jensen, 2001). Studies of cormorant predation in the Great Lakes have suggested that predation is not significant to the sport fishes in the Great Lakes (Diana et al., 2006). However in combination with the overfishing occurring at LLB, there is reason to suspect that the cormorant population may have an impact on the population of sport fishes.

The EFs observed for PCB 149 in northern pike filet tissue were not statistically different from the EFs of constituents of the lower food web; however the difference in EFs between northern pike liver samples was statistically different from that of yellow perch. All fish in this study exhibited racemic EFs of PCB 183. This observation is consistent with the observation that PCBs lacking both vicinal hydrogen atoms have low metabolic capability via CYP-mediated metabolism (Kannan et al., 1995). Our racemic EFs of PCB 183 indicate that little to no enantioselective bioprocessing is occurring in LLB fish. This does not rule out the occurrence of nonenantioselective metabolism, however, because PCB 183 was not detected in constituents at lower trophic levels in LLB, we cannot conclude that PCB 183 is being eliminated in northern pike.

Similar PCB 91 EFs were observed in forage fish in Lake Hartwell, SC, indicating depletion of the first eluting enantiomer of PCB 91 in bluegill (*Lepomis macrochirus*) (Wong et al., 2001). Enantiomer enrichment of PCBs 95, 136, and 149 appears to occur in a similar direction in Lake Hartwell as in LLB for top predator fish.

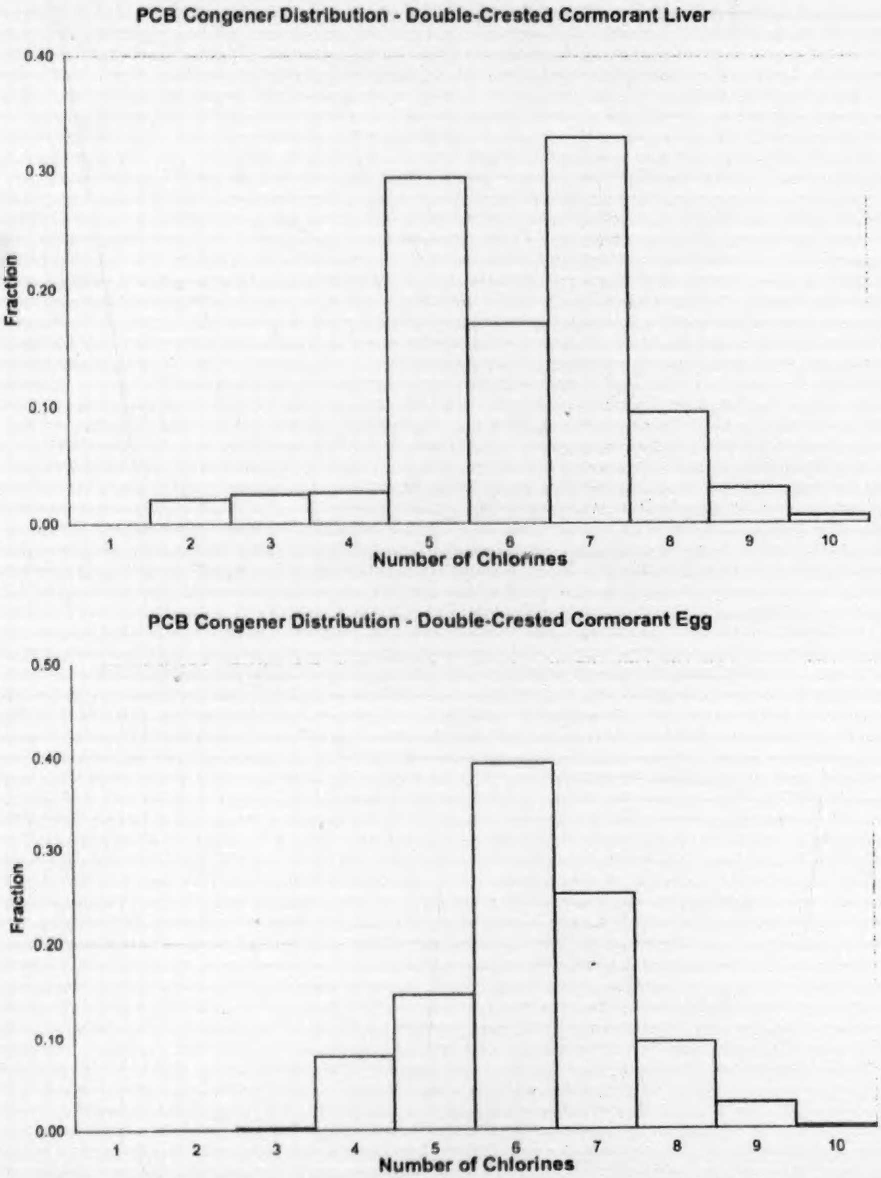
There was no statistically significant relationship between EFs of chiral PCB congeners and fork length in northern pike (all $p > 0.05$). Nonracemic EFs have been shown to be indicative of gender-dependent (Karlsson et al., 2000) and age-dependent (Hoekstra et al., 2002) enantioselective processes in Atlantic cod (*Gadhus morhua*) and in cetaceans, respectively. Our results also cannot confirm a relationship between PCB concentrations and EFs for chiral PCB congeners.

3.4.3. Chiral PCBs in Double-Crested Cormorant

Total PCB concentrations (Tables 1-2) observed in cormorant eggs are consistent with previous research on the species, with previously reported concentrations on the order of 3.8 μg/g in eggs from the West coast of Canada (Harris et al., 2003; Harris et al., 2005), and 380-7900 ng/g, wet weight in eggs from Lake Michigan (Kannan et al., 2001). Cormorant egg samples taken previously from Alberta had similar concentrations of 2.22 μg/g (Somers et al., 1993). Similar PCB congener profiles were also observed in this study (Kannan et al., 2001). Concentrations of total PCBs at this level have not been shown to induce toxic effects on adult birds, and there was also no correlation between PCB concentration and egg shell thickness or egg mortality at this level of PCB contamination in Alberta double-crested cormorants (Somers et al., 1993), as well as in great cormorants (*Phalacrocorax carbo sinensis*) in four studied wetlands in Greece . Concentrations on this order of magnitude suggest that they have a negligible impact on the environment of the wetlands studied in wetlands observed in Greece (Konstantinou et al., 2000). The concentrations of total PCBs reported in LLB are suspected to be as a result of bioaccumulation from the local diet, which is supported by previous research on the double-crested cormorant eggs and tissue in the province of Alberta (Somers et al., 1993). The significant bioaccumulation of PCBs exhibited from the local diet (Somers et al., 1993), relatively low mortality rates of chicks, (~25%) as studied in a similar-latitude lake in Saskatchewan (Kuiken et al., 1999), suggested that the double crested cormorant may be a significant vector in the removal of total PCB burden from Lac La Biche.

The presence of nonracemic PCB 45 in DCCO eggs is surprising, given the racemic EFs observed in adult bird livers, and chick tissues. There appears to be rapid elimination of the low-chlorinated congeners in the double-crested cormorant adults, therefore the presence of PCB 45 may be indicative of the concentrations found in the mother birds. In studies of maternal transfer of OCs to eggs in the glaucous gull, OCs with a lower K_{ow} were preferentially transferred to eggs whereas chemicals with higher K_{ow} were preferentially retained in the mother (Verreault et al., 2006). Congener profiles in this study are consistent with this observation (Figure 34). This may also account for the relatively lower concentrations of PCBs 149 and 183 observed in cormorant eggs compared to the adult birds. The nonracemic EFs observed may be as a result of stereoselective transfer of PCB 45 from mother to egg, however there is not enough data to confirm this hypothesis. The dynamics of possible enantioselective transfer of PCBs between mother and egg in the double-crested cormorant based on the results in this study are nonetheless interesting and warrant further investigation in future studies.

The nonracemic EFs of PCB 183 in the double-crested cormorant may also indicate the occurrence of stereoselective biotransformation based on racemic EFs in the lower food web. There are little data reported on enantioselective biotransformation of chiral PCB congeners specifically in the double-crested cormorant. There are statistical differences between the EFs of PCB 183 between top predator fish (northern pike and walleye), and double-crested cormorant. This difference is not significant for other congeners, but suggests that PCB 183 may have a different fate than other chiral congeners in the LLB food web. Group I congeners such as PCB 183 are not easily metabolized via CYP-1A and CYP-2B metabolic pathways because of the lack of adjacent vicinal hydrogen atoms on the biphenyl backbone (Boon et al., 1989). These results suggest that PCB 183 is being biotransformed by the cormorant, potentially by a different metabolic pathway than fish.


PCB Congener Distribution - Double-Crested Cormorant Liver

PCB Congener Distribution - Double-Crested Cormorant Egg

Figure 33: Homolog profiles of PCBs in double crested cormorant liver and egg samples in LLB.

In seabirds of the Northwater Polynya, enrichment of the (-)-enantiomer on PCBs 95 and 149 was reported for dovekie (*Alle alle*), thick-billed murre (*Uria lomvia*), black guillemot (*Cepphus grille*), northern fulmar (*Fulmaris glucialis*), ivory gull (*Pagophila eburnea*), black-legged kittiwake (*Rissa tridactyla*), and glaucous gull (*Larus hyperboreus*) (Warner et al., 2005). Enrichment of the (-)-enantiomer of PCB 149 in the double-crested cormorant in LLB may be as a result of several factors. Because the EFs of PCB 149 in yellow perch are racemic, stereoselective biotransformation may be occurring. Vicinal meta-para hydrogen atoms on PCB 149 and 95 make them susceptible to cytochrome CYP2B metabolism (Boon et al., 1989). Another hypothesis is the enantiomer profiles may be due to uptake of nonracemic PCBs via diet from wintering areas at lower latitudes (Somers et al., 1993; Glahn et al., 1995). Significant enrichment of the (-)-enantiomer of polybrominated biphenyl (PBB) 149 was observed in eggs of the white-tailed sea eagle (*Haliaeetus albicilla*) in Norway (EF=0.42) (von der Recke et al., 2005). In cormorant samples in LLB, EFs of analogous PCB 149 also indicate significant enrichment of the (-)-enantiomer, however at a much larger magnitude (EF=0.179). The discrepancies between these EFs may be due to variation in metabolic pathways between species, or due to potential differences between metabolic kinetics of PCBs and PBBs.

The EFs of chiral PCBs in cormorant eggs are statistically different from EFs observed in both chick and adult cormorant breast tissue for PCBs 95 and 149. These differences are not significant between liver tissue, suggesting that the enantioselective biotransformation of these congeners is tissue specific, and that maternal transfer of these congeners may also be stereoselective.

3.5. Conclusions

Polychlorinated biphenyls were detected in the biota of the aquatic food web of Lac La Biche. Concentrations detected in the three basins indicate that atmospheric deposition is the source of the PCB contamination. Our results demonstrate that biomagnification of PCBs is occurring in the aquatic food web of Lac La Biche. At the same time, nonracemic EFs of chiral PCBs indicate that bioprocessing of these xenobiotic congeners is also occurring throughout the food web in predatory fishes and cormorants. Double-crested cormorants have significantly higher PCB concentrations than fish in LLB, likely from wintering in more polluted environments, and also higher metabolic capacity for the elimination of these compounds. This may imply that the migratory population of cormorants in LLB is serving as another vector for the removal of PCBs from the LLB ecosystem, one which did not exist in the past, as a result of a lower cormorant population. In addition, due to the migratory nature of the cormorant, there may be significant elimination of PCBs from the lake, by the physical removal of contaminants. Tissue specific differences in EF were also observed in northern pike and cormorant tissues. Thus, there is a possibility of stereoselective maternal transfer of chiral pollutants to eggs in cormorants. These results are exciting, and warrant further investigation.

Chapter 4 - Future Research and Directions

As stated in the introduction to Chapter Three, this study has provided a "snapshot" of the contaminant profile of LLB for the summer of 2004. Since this time, population control measures, such as the oiling of cormorant eggs, and cormorant culling occurred. Once population changes are observed, a future study of this magnitude will be completed, providing a dynamic picture of the contaminant trends in LLB. Changes in the composition of the LLB food wen as a result of population control of cormorants may change the overall fate for persistent organic pollutants in the LLB watershed.

These population changes in cormorants may alter the overall composition of enantiomers of chiral PCBs, because DCCO have a greater capacity to biotransform chiral PCBs. In addition, the DCCO is a migratory species. If the population of DCCO were to decline, fewer PCBs will be arriving from warmer climates where the birds spend winter months. Because of the large PCB manufacturing of these areas in the past, the contamination is generally more severe. In addition, fewer PCBs will be "flying south" for the winter, therefore, the PCB flux will be relatively contained within the LLB watershed.

In addition, future studies of tissue-specific contaminant concentrations may be performed in the double-crested cormorant. A large sample size of DCCO may be collected to observe the enantiomeric fractions of chiral PCBs in liver, muscle, adipose, brain, and lung tissue in order to determine the capabilities of biotranformation of chiral PCBs in various cormorant tissues. This may provide insight towards the total biotransformation of chiral PCB enantiomers in the DCCO.

This study has also shown that the DCCO can efficiently biotransform chiral PCBs. CYP1A- and CYP2B-like metabolism have been observed in shorebirds and double crested cormorants (Buckman et al., 2004). These metabolic pathways generate hydroxylated and methyl sulfonyl PCBs as metabolites. In some cases, these metabolites themselves are persistent and bioaccumulate in biota. Chiral metabolites may also be formed, and food web studies like this one may be of interest. Refinement of the methods for the extraction and analysis of PCB metabolites needs to occur, and analysis of these molecules should be performed on an insurument with greater sensitivity than a quadropole MS operating in EI mode.

An exciting direction that this study may take is monitoring the potential enantioselective maternal transfer of chiral contaminants from female DCCO to their eggs. Future sampling, obtaining larger data sets will give greater insights towards enantioselective processes occurring in DCCO. Enrichment of the first eluting enantiomer of PCB 95 in the DCCO may be used to confirm this hypothesis.

There are several ways that metabolites of chiral PCBs may be studied. An *in vitro* study may be performed in order to determine the stereoselective formation of chiral methyl-sulfonated- and hydroxylated- PCBs in laboratory animals. Such a study would provide insight into the means of metabolite formation, as well as the EF direction of metabolite formation. One question that may be asked is: "Does depletion of the (-)-enantiomer of PCB 149 result in the formation of the (+) or (-)- enantiomer of the methylsulfonated- or hydroxylated- metabolite of PCB 149"?

There are many emerging pollutants in the world, and many of these molecules are chiral. As technology advances, providing researchers means to analyse for contaminants at ultra-trace concentrations in biota, the archived samples from this study will allow the food web dynamics of other pollutants in the biota of LLB to be determined for a wide range of pollutants.

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Appendix 1 - Sample Collection Information

The following legend applies apply to the sample ID tabulated in appendices 1-4:

Abbreviation		Abbreviation	
CISC	Cisco	**SPSH**	Spot-tail Shiner
DCCO	Double-crested Cormorant	**TB**	Town Basin
EB	East Basin	**WB**	West Basin
LIV	Liver	**WALL**	Walleye
LKWH	Lake Whitefish	**WHSC**	White Sucker
NRPK	Northern Pike	**YLPR**	Yellow Perch

	CISC	**CISC**	**CISC**	**CISC**	**CISC LIV**	**CISC LIV**	**CISC LIV**	**CISC LIV**	**DCCO**
Sample ID	WBCISC1	WBCISC2	179CISC	215CISC	CISCLIV1	CISCLIV2	179CISCL	215CISCL	DCCO060718
Fork Length (mm)	241	279	179	215	241	279	179	215	
Mass Extracted	10.8415	9.0209	10.7625	10.8097	0.9968	1.8703	0.8891	0.8148	9.7472
%Lipid	1.9530	0.8875	2.9283	4.8887	4.5748	5.1043	5.4386	6.7523	6.7174
Mass Lipid	0.2117	0.0801	0.3152	0.5285	0.0456	0.0955	0.0484	0.0550	0.6548
%Recovery 204	59.70%	61.70%	102.50%	100.70%	63.10%	94.00%	94.20%	92.50%	135.30%

	DCCO	DCCO	DCCO	DCCO Chick	DCCO Chick	DCCO Chick	Chick Liver	Chick Liver	Chick Liver
Sample ID	DCCO060727	DCCO A	DCCO B	CHICK	DCCO 1472	DCCO 637	CHICKLIV	DCCO1111	DCCO637
Fork Length (mm)				708 g	1472 g	637 g	708 g	1111 g	637 g
Mass Extracted	6.1188	8.3886	8.9060	4.3345	8.3155	6.8193	6.0958	5.8695	5.4242
%Lipid	7.2250	7.1788	3.9524	2.2252	1.8382	2.3599	3.1462	2.0430	3.8188
Mass Lipid	0.4421	0.6022	0.3520	0.0964	0.1529	0.1609	0.1918	0.1199	0.2071
%Recovery 204	123.3%	63.2%	99.0%	92.8%	97.2%	101.9%	92.3%	133.9%	134.2%

	Chick Liver	DCCO EGG	DCCO EGG	DCCO EGG	DCCO LIVER	DCCO LIVER	DCCO LIVER	DCCO LIVER	LKWH
Sample ID	DCCO 1472 LIVER	EGG 060519	EGG 060710	EGG 060727	COLIV060718	COLIV060727	DCCOALIV	DCCOBLIV	LKWHA
Fork Length (mm)	1472 g	43.5 g	44.5 g	50.6 g					434
Mass Extracted	9.3711	42.5286	43.2209	49.5661	7.8111	5.0880	10.2435	8.3763	11.4854
%Lipid	4.8720	4.4873	5.4198	3.9765	3.1658	5.6654	4.2895	5.2563	1.8985
Mass Lipid	0.4566	1.9084	2.3425	1.9710	0.2473	0.2883	0.4394	0.4403	0.2181
%Recovery 204	91.7%	372.8%	213.0%	174.0%	105.7%	80.1%	74.5%	73.3%	77.8%

	LKWH	LKWH	LKWH	LKWH Liver	LKWH Liver	NRPK	NRPK	NRPK	NRPK
Sample ID	LKWHB	LKWHC	434 LKWH	LKWH434L	LKWH492L	NRPK A	NRPK B	NRPK C	NRPK 584
Fork Length (mm)	446	492	434	434	492	715	626	672	584
Mass Extracted	9.3552	9.6593	9.6594	6.6732	9.9752	10.4353	11.9589	9.0786	8.5101
%Lipid	1.3796	2.2112	3.2112	3.9109	14.6558	0.9004	0.7784	0.5429	0.4470
Mass Lipid	0.1291	0.2136	0.3102	0.2610	1.4619	0.0939	0.1076	0.0817	0.0766
%Recovery 204	69.9%	73.8%	86.8%	86.3%	88.9%	154.8%	246.8%	101.5%	67.8%

	NRPK	NRPK	NRPK	NRPK	NRPK	NRPK	NRPK	NRPK	NRPK
Sample ID	NRPK 598	NRPK 612	NRPK 614	660 NRPK	675 NRPK	573 NRPK	580 NRPK	620 NRPK	NRPK 491
Fork Length (mm)	598	612	614	660	675	573	580	620	491
Mass Extracted	8.8024	8.9635	9.4970	5.8624	5.4050	6.5291	8.4966	7.6299	12.5085
%Lipid	0.7989	0.5011	0.5248	0.5591	0.7826	15.9237	11.3118	7.6192	0.5351
Mass Lipid	0.0792	0.0807	0.0855	0.0328	0.0423	1.0397	0.9611	0.5813	0.0669
%Recovery 204	77.5%	72.8%	70.7%	95.3%	100.9%	114.3%	107.9%	90.9%	98.2%

	NRPK	NRPK	NRPK	NRPK	NRPK LIVER	NRPK LIVER	NRPK LIVER	NRPK LIVER	NRPK LIVER
Sample ID	NRPK 742	NRPK 620	NRPK 815	NRPK 638	NRPKL1	660NRPKLIV	675NRPKLIV	NRPK742L	NRPK620L2
Fork Length (mm)	742	620	815	638	715	660	675	742	620
Mass Extracted	12.0841	24.4254	19.3515	4.8177	7.8209	6.6779	5.0616	10.6816	12.3829
%Lipid	0.5756	0.9090	0.5128	0.8581	8.0012	6.4389	7.7236	12.2151	9.4269
Mass Lipid	0.0696	0.2220	0.0992	0.0413	0.6257	0.4300	0.3909	1.3048	1.1673
%Recovery 204	232.9%	81.6%	85.7%	76.4%	75.5%	98.4%	96.7%	88.2%	101.3%

	NRPK LIVER	NRPK LIVER	SNAIL	SPSH	SPSH	SPSH	WALL	WALL	WALL LIVER
Sample ID	NRPK815L	NRPK638L	TBSN	WBSPSH	WBSPSH2	SPSH	WALL485-2	WALL540	WALL485-2
Fork Length (mm)	815	638	composite	minnow	minnow	composite	485	540	485
Mass Extracted	8.9140	5.0031	10.2618	10.3969	9.5313	12.5457	7.1352	6.0145	7.6873
%Lipid	8.0724	6.1637	0.5779	2.8450	1.6718	1.2637	1.1882	0.8372	5.1410
Mass Lipid	0.7196	0.3084	0.0593	0.2958	0.1593	0.1585	0.0848	0.0504	0.3952
%Recovery 204	76.8%	67.9%	111.0%	99.3%	99.4%	121.1%	84.7%	120.3%	96.0%

	WALL LIVER	WHSC	YLPR	YLPR	YLPR	YLPR	YLPR	YLPR	YLPR
Sample ID	WALL 540	WHSC060519	EBYLPR	WBYLPR	215YLPR	YLPREB	YLPRTB	YLPRTBMAY	YLPRWB
Fork Length (mm)	540	450	2 fish	2 fish	215	20 fish	20 fish	11 fish	30 fish
Mass Extracted	5.0138	15.6804	12.5908	17.0657	9.9751	9.4576	10.7645	10.4088	9.8760
%Lipid	8.3331	3.7489	2.7327	2.6109	5.1935	3.4347	2.5150	1.6828	2.5469
Mass Lipid	0.4178	0.5878	0.3441	0.4456	0.5181	0.3248	0.2707	0.1752	0.2515
%Recovery 204	82.4%	91.9%	101.1%	88.7%	94.2%	111.3%	130.0%	130.0%	116.7%

	YLPR	YLPR	YLPR	YLPR LIV	YLPR LIV
Sample ID	YLPR EB A	YLPR EB B	YLPR WB	215YLPRL	YLPRLIV
Fork Length (mm)	composite	composite	composite	215	composite
Mass Extracted	13.0768	12.4867	14.0837	1.3088	2.9521
%Lipid	2.9268	2.8930	1.5137	5.4740	3.9333
Mass Lipid	0.3827	0.3612	0.2132	0.0716	0.1161
%Recovery 204	98.6%	96.3%	96.0%	85.1%	171.4%

Appendix 2 - Chiral PCB Raw Data

	Species	CISC	CISC	CISC	CISC
	Sample ID	WBCISC1	WBCISC2	179CISC	215CISC
PCB 45	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 91	Measured Conc. (ng)	0.30	ND	0.08	0.06
	Concenration (ng/g)	0.50	ND	0.08	0.06
	Lipid Normalized Concentration (ng/g_{lipid})	0.15	ND	0.03	0.01
	EF	0.58	NA	0.47	0.44
PCB 95	Measured Conc. (ng)	1.23	0.97	0.43	0.33
	Concenration (ng/g)	2.06	1.57	0.42	0.33
	Lipid Normalized Concentration (ng/g_{lipid})	0.63	1.09	0.15	0.07
	EF	0.51	0.51	0.49	0.49
PCB 136	Measured Conc. (ng)	0.48	ND	0.23	0.21
	Concenration (ng/g)	0.81	ND	0.22	0.21
	Lipid Normalized Concentration (ng/g_{lipid})	0.41	ND	0.08	0.04
	EF	0.50	NA	0.41	0.42
PCB 149	Measured Conc. (ng)	3.04	2.65	1.01	0.97
	Concenration (ng/g)	5.10	4.29	0.98	0.97
	Lipid Normalized Concentration (ng/g_{lipid})	1.56	2.98	0.34	0.20
	EF	0.51	0.49	0.47	0.47
PCB 174	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA

	Species Sample ID	CISC LIV CISCLIV1	CISC LIV CISCLIV2	CISC LIV 179CISCL	CISC LIV 215CISCL
PCB 45	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 91	**Measured Conc. (ng)**	0.25	ND	ND	ND
	Concenration (ng/g)	0.40	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	0.05	ND	ND	ND
	EF	0.42	NA	NA	NA
PCB 95	**Measured Conc. (ng)**	1.18	ND	0.63	0.47
	Concenration (ng/g)	1.87	ND	0.67	0.51
	Lipid Normalized Concentration (ng/g_{lipid})	0.26	ND	0.12	0.07
	EF	0.53	NA	0.51	0.52
PCB 136	**Measured Conc. (ng)**	0.81	ND	ND	ND
	Concenration (ng/g)	1.29	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	0.28	ND	ND	ND
	EF	0.47	NA	NA	NA
PCB 149	**Measured Conc. (ng)**	2.94	ND	0.99	0.63
	Concenration (ng/g)	4.65	ND	1.05	0.68
	Lipid Normalized Concentration (ng/g_{lipid})	0.64	ND	0.18	0.09
	EF	0.50	NA	0.48	0.46
PCB 174	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	**Measured Conc. (ng)**	ND	ND	ND	1.05
	Concenration (ng/g)	ND	ND	ND	1.13
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	0.16
	EF	NA	NA	NA	0.49

	Species	DCCO	DCCO	DCCO	DCCO
	Sample ID	**DCCO060718**	**DCCO060727**	**DCCO A**	**DCCO B**
PCB 45	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 91	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 95	**Measured Conc. (ng)**	0.05	0.05	ND	0.06
	Concenration (ng/g)	0.04	0.04	ND	0.07
	Lipid Normalized Concentration (ng/g_{lipid})	0.01	0.01	ND	0.02
	EF	0.55	0.48	NA	0.46
PCB 136	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 149	**Measured Conc. (ng)**	0.61	0.18	ND	0.50
	Concenration (ng/g)	0.45	0.14	ND	0.50
	Lipid Normalized Concentration (ng/g_{lipid})	0.09	0.02	ND	0.13
	EF	0.47	0.38	NA	0.50
PCB 174	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	**Measured Conc. (ng)**	3.78	40.91	9.44	46.61
	Concenration (ng/g)	2.79	33.19	14.93	47.07
	Lipid Normalized Concentration (ng/g_{lipid})	0.56	5.66	1.31	11.79
	EF	0.55	0.66	0.61	0.71

	Species	DCCO Chick	DCCO Chick	DCCO Chick	DCCO Chick Liver
	Sample ID	CHICK	DCCO 1472	DCCO 637	CHICKLIV
PCB 45	Measured Conc. (ng)	0.20	ND	ND	ND
	Concenration (ng/g)	0.22	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	0.09	ND	ND	ND
	EF	0.53	NA	NA	NA
PCB 91	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 95	Measured Conc. (ng)	0.07	ND	ND	0.04
	Concenration (ng/g)	0.08	ND	ND	0.04
	Lipid Normalized Concentration (ng/g_{lipid})	0.03	ND	ND	0.01
	EF	0.49	NA	NA	0.49
PCB 136	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 149	Measured Conc. (ng)	0.17	ND	ND	0.44
	Concenration (ng/g)	0.18	ND	ND	0.48
	Lipid Normalized Concentration (ng/g_{lipid})	0.07	ND	ND	0.14
	EF	0.50	NA	NA	0.38
PCB 174	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	Measured Conc. (ng)	0.91	2.76	0.27	1.87
	Concenration (ng/g)	0.98	2.84	0.26	2.03
	Lipid Normalized Concentration (ng/g_{lipid})	0.41	1.50	0.11	0.59
	EF	0.56	0.64	0.72	0.65

	Species	DCCO Chick Liver	DCCO Chick Liver	DCCO Chick Liver	DCCO EGG
	Sample ID	DCCO1111	DCCO637	DCCO 1472 LIVER	EGG 060519
PCB 45	**Measured Conc. (ng)**	ND	ND	ND	0.40
	Concenration (ng/g)	ND	ND	ND	0.11
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	0.09
	EF	NA	NA	NA	0.38
PCB 91	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 95	**Measured Conc. (ng)**	ND	ND	0.03	0.02
	Concenration (ng/g)	ND	ND	0.03	0.01
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	0.01	0.00
	EF	NA	NA	0.49	0.39
PCB 136	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 149	**Measured Conc. (ng)**	0.40	ND	0.08	1.56
	Concenration (ng/g)	0.30	ND	0.09	0.42
	Lipid Normalized Concentration (ng/g_{lipid})	0.19	ND	0.02	0.35
	EF	0.26	NA	0.49	0.11
PCB 174	**Measured Conc. (ng)**	ND	ND	ND	2.47
	Concenration (ng/g)	ND	ND	ND	0.66
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	0.55
	EF	NA	NA	NA	0.68
PCB 183	**Measured Conc. (ng)**	ND	0.66	0.76	780.15
	Concenration (ng/g)	ND	0.50	0.83	209.28
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.17	0.16	173.86
	EF	NA	0.58	0.72	0.63

	Species	DCCO EGG	DCCO EGG	DCCO LIVER	DCCO LIVER
	Sample ID	EGG 060710	EGG 060727	COLIV060718	COLIV060727
PCB 45	Measured Conc. (ng)	0.41	ND	ND	ND
	Concenration (ng/g)	0.19	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	0.08	ND	ND	ND
	EF	0.42	NA	NA	NA
PCB 91	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 95	Measured Conc. (ng)	0.03	0.04	ND	0.07
	Concenration (ng/g)	0.02	0.02	ND	0.09
	Lipid Normalized Concentration (ng/g_{lipid})	0.01	0.01	ND	0.01
	EF	0.36	0.44	NA	0.26
PCB 136	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 149	Measured Conc. (ng)	1.90	0.59	0.89	0.24
	Concenration (ng/g)	0.89	0.34	0.84	0.30
	Lipid Normalized Concentration (ng/g_{lipid})	0.35	0.15	0.28	0.04
	EF	0.12	0.23	0.45	0.22
PCB 174	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	Measured Conc. (ng)	241.03	244.98	1.80	24.30
	Concenration (ng/g)	113.16	140.82	1.70	30.34
	Lipid Normalized Concentration (ng/g_{lipid})	44.47	61.61	0.57	4.29
	EF	0.57	0.58	0.64	0.66

	Species	DCCO LIVER	DCCO LIVER	LKWH	LKWH
	Sample ID	DCCOALIV	DCCOBLIV	LKWHA	LKWHB
PCB 45	Measured Conc. (ng)	0.07	0.07	ND	ND
	Concenration (ng/g)	0.10	0.09	ND	ND
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	0.02	0.01	ND	ND
	EF	0.47	0.49	NA	NA
PCB 91	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	ND	ND	ND	ND
	EF	NA	NA	ND	ND
PCB 95	Measured Conc. (ng)	0.05	0.05	0.10	0.08
	Concenration (ng/g)	0.06	0.07	0.13	0.12
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	0.01	0.01	0.05	0.06
	EF	0.45	0.49	0.52	0.56
PCB 136	Measured Conc. (ng)	ND	ND	0.11	0.18
	Concenration (ng/g)	ND	ND	0.15	0.26
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	ND	ND	0.08	0.19
	EF	NA	NA	0.51	0.47
PCB 149	Measured Conc. (ng)	0.36	0.21	0.81	0.35
	Concenration (ng/g)	0.49	0.28	1.05	0.50
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	0.08	0.04	0.43	0.25
	EF	0.15	0.23	0.44	0.47
PCB 174	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	Measured Conc. (ng)	9.52	25.37	ND	ND
	Concenration (ng/g)	12.78	34.59	ND	ND
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	2.22	4.83	ND	ND
	EF	0.69	0.77	NA	NA

	Species	LKWH	LKWH	LKWH Liver	LKWH Liver
	Sample ID	LKWHC	434 LKWH	LKWH434L	LKWH492L
PCB 45	Measured Conc. (ng)	0.15	ND	0.08	0.07
	Concenration (ng/g)	0.20	ND	0.09	0.08
	Lipid Normalized Concentration (ng/g_{lipid})	0.07	ND	0.02	0.01
	EF	0.48	NA	0.47	0.47
PCB 91	Measured Conc. (ng)	0.05	ND	0.02	ND
	Concenration (ng/g)	0.06	ND	0.02	ND
	Lipid Normalized Concentration (ng/g_{lipid})	0.02	ND	0.01	ND
	EF	0.46	ND	0.37	NA
PCB 95	Measured Conc. (ng)	0.26	0.10	0.08	0.49
	Concenration (ng/g)	0.35	0.12	0.09	0.55
	Lipid Normalized Concentration (ng/g_{lipid})	0.12	0.03	0.02	0.03
	EF	0.51	0.54	0.49	0.38
PCB 136	Measured Conc. (ng)	0.14	ND	0.06	0.12
	Concenration (ng/g)	0.18	ND	0.07	0.14
	Lipid Normalized Concentration (ng/g_{lipid})	0.08	ND	0.02	0.01
	EF	0.56	ND	0.50	0.42
PCB 149	Measured Conc. (ng)	0.58	0.36	0.26	0.63
	Concenration (ng/g)	0.79	0.41	0.30	0.71
	Lipid Normalized Concentration (ng/g_{lipid})	0.26	0.11	0.07	0.04
	EF	0.50	0.48	0.48	0.39
PCB 174	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA

	Species	NRPK	NRPK	NRPK	NRPK
	Sample ID	NRPK A	NRPK B	NRPK C	NRPK 584
PCB 45	**Measured Conc. (ng)**	2.24	1.82	1.97	0.05
	Concenration (ng/g)	1.44	0.74	1.94	0.08
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	2.49	2.02	2.19	0.06
	EF	0.49	0.50	0.49	0.49
PCB 91	**Measured Conc. (ng)**	0.47	0.36	0.34	0.04
	Concenration (ng/g)	0.30	0.15	0.34	0.06
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	0.52	0.40	0.38	0.05
	EF	0.54	0.56	0.57	0.39
PCB 95	**Measured Conc. (ng)**	1.28	0.92	1.12	0.16
	Concenration (ng/g)	0.83	0.37	1.10	0.24
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	1.42	1.02	1.24	0.18
	EF	0.51	0.50	0.51	0.51
PCB 136	**Measured Conc. (ng)**	0.80	0.58	0.67	0.18
	Concenration (ng/g)	0.51	0.24	0.66	0.27
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	0.57	0.26	0.73	0.30
	EF	0.50	0.49	0.50	0.50
PCB 149	**Measured Conc. (ng)**	3.06	2.08	2.56	0.64
	Concenration (ng/g)	1.98	0.84	2.53	0.94
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	3.40	2.31	2.85	0.71
	EF	0.49	0.49	0.49	0.49
PCB 174	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration ($\text{ng/g}_{\text{lipid}}$)	ND	ND	ND	ND
	EF	NA	NA	NA	NA

	Species	NRPK	NRPK	NRPK	NRPK
	Sample ID	NRPK 598	NRPK 612	NRPK 614	660 NRPK
PCB 45	**Measured Conc. (ng)**	ND	0.22	0.70	0.08
	Concenration (ng/g)	ND	0.30	0.99	0.08
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.24	0.78	0.14
	EF	NA	0.50	0.51	0.46
PCB 91	**Measured Conc. (ng)**	ND	ND	0.10	ND
	Concenration (ng/g)	ND	ND	0.15	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	0.12	ND
	EF	NA	NA	0.48	NA
PCB 95	**Measured Conc. (ng)**	ND	0.24	0.21	0.06
	Concenration (ng/g)	ND	0.33	0.29	0.06
	Lipid Normalized Concentration (ng/g_{lipid})	ND		0.23	0.10
	EF	NA	0.47	0.48	0.48
PCB 136	**Measured Conc. (ng)**	ND	0.14	0.13	ND
	Concenration (ng/g)	ND	0.19	0.18	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.21	0.20	ND
	EF	NA	0.47	0.49	NA
PCB 149	**Measured Conc. (ng)**	ND	1.08	3.36	0.09
	Concenration (ng/g)	ND	1.48	4.75	0.09
	Lipid Normalized Concentration (ng/g_{lipid})	ND	1.20	3.73	0.16
	EF	NA	0.48	0.46	0.48
PCB 174	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	**Measured Conc. (ng)**	ND	1.57	ND	ND
	Concenration (ng/g)	ND	2.16	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.10	ND	ND
	EF	NA	0.52	NA	NA

	Species Sample ID	NRPK 675 NRPK	NRPK 573 NRPK	NRPK 580 NRPK	NRPK 620 NRPK
PCB 45	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 91	**Measured Conc. (ng)**	ND	0.20	0.34	ND
	Concenration (ng/g)	ND	0.17	0.31	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.01	0.03	ND
	EF	NA	0.39	0.41	NA
PCB 95	**Measured Conc. (ng)**	0.07	0.61	9.48	0.17
	Concenration (ng/g)	0.07	0.53	8.78	0.18
	Lipid Normalized Concentration (ng/g_{lipid})	0.09	0.04	0.84	0.02
	EF	0.46	0.48	0.48	0.53
PCB 136	**Measured Conc. (ng)**	ND	0.26	4.29	ND
	Concenration (ng/g)	ND	0.22	3.97	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.01	0.35	ND
	EF	NA	0.43	0.43	NA
PCB 149	**Measured Conc. (ng)**	1.37	1.82	3.41	0.58
	Concenration (ng/g)	1.36	1.59	3.16	0.64
	Lipid Normalized Concentration (ng/g_{lipid})	1.75	0.11	0.30	0.08
	EF	0.40	0.44	0.40	0.41
PCB 174	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	**Measured Conc. (ng)**	ND	1.22	1.50	2.79
	Concenration (ng/g)	ND	1.07	1.39	3.07
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.08	0.13	0.37
	EF	NA	0.51	0.52	0.48

	Species Sample ID	NRPK NRPK 491	NRPK NRPK 742	NRPK NRPK 620	NRPK NRPK 815
PCB 45	**Measured Conc. (ng)**	ND	0.24	ND	0.06
	Concenration (ng/g)	ND	0.11	ND	0.07
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.42	ND	0.12
	EF	NA	0.47	NA	0.56
PCB 91	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 95	**Measured Conc. (ng)**	ND	0.12	0.40	0.10
	Concenration (ng/g)	ND	0.05	0.49	0.11
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.20	0.44	0.19
	EF	NA	0.50	0.53	0.51
PCB 136	**Measured Conc. (ng)**	ND	0.13	ND	ND
	Concenration (ng/g)	ND	0.06	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.10	ND	ND
	EF	NA	0.44	NA	NA
PCB 149	**Measured Conc. (ng)**	0.68	0.63	1.22	0.32
	Concenration (ng/g)	0.69	0.27	1.49	0.37
	Lipid Normalized Concentration (ng/g_{lipid})	1.26	1.09	1.34	0.62
	EF	0.49	0.48	0.37	0.32
PCB 174	**Measured Conc. (ng)**	ND	ND	0.13	ND
	Concenration (ng/g)	ND	ND	0.16	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	0.14	ND
	EF	NA	NA	0.51	NA
PCB 183	**Measured Conc. (ng)**	0.78	ND	0.42	ND
	Concenration (ng/g)	0.79	ND	0.51	ND
	Lipid Normalized Concentration (ng/g_{lipid})	1.45	ND	0.46	ND
	EF	0.47	NA	0.55	NA

	Species	NRPK	NRPK LIVER	NRPK LIVER	NRPK LIVER
	Sample ID	NRPK 638	NRPKL1	660NRPKLIV	675NRPKLIV
PCB 45	Measured Conc. (ng)	ND	1.62	ND	1.05
	Concenration (ng/g)	ND	2.15	ND	1.08
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.20	ND	0.14
	EF	NA	0.50	NA	0.50
PCB 91	Measured Conc. (ng)	ND	0.45	ND	0.09
	Concenration (ng/g)	ND	0.60	ND	0.09
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.06	ND	0.01
	EF	NA	0.46	NA	0.43
PCB 95	Measured Conc. (ng)	ND	1.39	ND	0.38
	Concenration (ng/g)	ND	1.84	ND	0.39
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.17	ND	0.05
	EF	NA	0.50	NA	0.56
PCB 136	Measured Conc. (ng)	ND	0.81	ND	0.11
	Concenration (ng/g)	ND	1.08	ND	0.11
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.13	ND	0.01
	EF	NA	0.46	NA	0.30
PCB 149	Measured Conc. (ng)	ND	4.14	0.15	1.31
	Concenration (ng/g)	ND	5.48	0.15	1.35
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.52	0.02	0.17
	EF	NA	0.45	0.43	0.30
PCB 174	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	Measured Conc. (ng)	ND	ND	0.84	2.72
	Concenration (ng/g)	ND	ND	0.85	2.81
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	0.13	0.35
	EF	NA	NA	0.51	0.52

	Species	NRPK LIVER	NRPK LIVER	NRPK LIVER	NRPK LIVER
	Sample ID	NRPK742L	NRPK620L2	NRPK815L	NRPK638L
PCB 45	Measured Conc. (ng)	0.27	ND	0.11	ND
	Concenration (ng/g)	0.30	ND	0.14	ND
	Lipid Normalized Concentration (ng/g_{lipid})	0.02	ND	0.01	ND
	EF	0.53	NA	0.52	NA
PCB 91	Measured Conc. (ng)	1.63	0.38	0.16	ND
	Concenration (ng/g)	1.85	0.37	0.20	ND
	Lipid Normalized Concentration (ng/g_{lipid})	0.13	0.04	0.02	ND
	EF	0.33	0.38	0.38	NA
PCB 95	Measured Conc. (ng)	1.59	1.99	0.64	0.17
	Concenration (ng/g)	1.81	1.96	0.84	0.25
	Lipid Normalized Concentration (ng/g_{lipid})	0.13	0.21	0.08	0.03
	EF	0.48	0.52	0.51	0.55
PCB 136	Measured Conc. (ng)	0.62	0.40	0.32	ND
	Concenration (ng/g)	0.71	0.40	0.41	ND
	Lipid Normalized Concentration (ng/g_{lipid})	0.06	0.04	0.05	ND
	EF	0.33	0.41	0.41	NA
PCB 149	Measured Conc. (ng)	7.73	4.47	2.41	0.24
	Concenration (ng/g)	8.77	4.41	3.13	0.36
	Lipid Normalized Concentration (ng/g_{lipid})	0.63	0.47	0.30	0.04
	EF	0.33	0.42	0.32	0.31
PCB 174	Measured Conc. (ng)	2.35	0.09	ND	ND
	Concenration (ng/g)	2.66	0.09	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	0.19	0.01	ND	ND
	EF	0.53	0.60	NA	NA
PCB 183	Measured Conc. (ng)	2.44	2.23	ND	ND
	Concenration (ng/g)	2.77	2.20	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	0.20	0.24	ND	ND
	EF	0.51	0.46	NA	NA

	Species	SNAIL	SPSH	SPSH	SPSH
	Sample ID	TBSN	WBSPSH	WBSPSH2	SPSH
PCB 45	Measured Conc. (ng)	ND	ND	ND	0.10
	Concenration (ng/g)	ND	ND	ND	0.08
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	0.08
	EF	NA	NA	NA	0.53
PCB 91	Measured Conc. (ng)	ND	0.02	ND	0.04
	Concenration (ng/g)	ND	0.02	ND	0.04
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.01	ND	0.04
	EF	NA	0.53	NA	0.54
PCB 95	Measured Conc. (ng)	0.93	0.09	1.20	0.11
	Concenration (ng/g)	0.83	0.09	1.21	0.09
	Lipid Normalized Concentration (ng/g_{lipid})	1.60	0.03	0.72	0.09
	EF	0.52	0.52	0.50	0.49
PCB 136	Measured Conc. (ng)	ND	0.01	0.77	ND
	Concenration (ng/g)	ND	0.01	0.77	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.00	0.46	ND
	EF	NA	0.47	0.47	NA
PCB 149	Measured Conc. (ng)	2.75	3.50	3.22	0.15
	Concenration (ng/g)	2.48	3.52	3.24	0.13
	Lipid Normalized Concentration (ng/g_{lipid})	4.76	1.23	1.93	0.12
	EF	0.50	0.48	0.52	0.46
PCB 174	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA

	Species	WALL	WALL	WALL LIVER	WALL LIVER
	Sample ID	WALL485-2	WALL540	WALL485-2	WALL 540
PCB 45	Measured Conc. (ng)	1.96	ND	0.12	ND
	Concenration (ng/g)	2.31	ND	0.12	ND
	Lipid Normalized Concentration (ng/g_{lipid})	1.65	ND	0.02	ND
	EF	0.60	NA	0.52	NA
PCB 91	Measured Conc. (ng)	ND	ND	0.03	ND
	Concenration (ng/g)	ND	ND	0.03	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	0.01	ND
	EF	NA	NA	0.52	NA
PCB 95	Measured Conc. (ng)	1.79	ND	0.18	0.12
	Concenration (ng/g)	2.11	ND	0.19	0.14
	Lipid Normalized Concentration (ng/g_{lipid})	1.50	ND	0.04	0.01
	EF	0.50	NA	0.49	0.49
PCB 136	Measured Conc. (ng)	ND	ND	0.15	0.10
	Concenration (ng/g)	ND	ND	0.15	0.12
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	0.03	0.01
	EF	NA	NA	0.49	0.52
PCB 149	Measured Conc. (ng)	2.46	0.67	2.46	0.70
	Concenration (ng/g)	2.91	0.56	2.57	0.84
	Lipid Normalized Concentration (ng/g_{lipid})	2.07	0.80	0.48	0.08
	EF	0.39	0.46	0.44	0.48
PCB 174	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	Measured Conc. (ng)	0.98	ND	ND	ND
	Concenration (ng/g)	1.15	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	0.82	ND	ND	ND
	EF	0.52	NA	NA	NA

	Species	WHSC	YLPR	YLPR	YLPR
	Sample ID	WHSC060519	EBYLPR	WBYLPR	215YLPR
PCB 45	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 91	**Measured Conc. (ng)**	0.12	0.06	ND	0.05
	Concenration (ng/g)	0.13	0.05	ND	0.05
	Lipid Normalized Concentration (ng/g_{lipid})	0.00	0.02	ND	0.01
	EF	0.42	0.53	NA	0.50
PCB 95	**Measured Conc. (ng)**	0.85	0.14	0.65	0.26
	Concenration (ng/g)	0.92	0.14	0.73	0.28
	Lipid Normalized Concentration (ng/g_{lipid})	0.02	0.05	0.25	0.05
	EF	0.50	0.50	0.50	0.49
PCB 136	**Measured Conc. (ng)**	0.27	0.02	0.54	0.15
	Concenration (ng/g)	0.30	0.02	0.61	0.16
	Lipid Normalized Concentration (ng/g_{lipid})	0.08	0.01	0.23	0.03
	EF	0.48	0.51	0.53	0.43
PCB 149	**Measured Conc. (ng)**	1.55	2.58	1.98	0.72
	Concenration (ng/g)	1.69	2.55	2.23	0.76
	Lipid Normalized Concentration (ng/g_{lipid})	0.04	0.94	0.76	0.14
	EF	0.54	0.50	0.47	0.49
PCB 174	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	**Measured Conc. (ng)**	0.97	ND	ND	ND
	Concenration (ng/g)	1.06	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	0.03	ND	ND	ND
	EF	NA	NA	NA	NA

	Species Sample ID	YLPR YLPREB	YLPR YLPRTB	YLPR YLPRTBMAY	YLPR YLPRWB
PCB 45	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 91	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 95	**Measured Conc. (ng)**	ND	0.08	0.09	0.13
	Concenration (ng/g)	ND	0.06	0.07	0.11
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.03	0.05	0.05
	EF	NA	0.47	0.54	0.53
PCB 136	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 149	**Measured Conc. (ng)**	ND	0.22	0.22	0.20
	Concenration (ng/g)	ND	0.17	0.17	0.17
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.09	0.13	0.08
	EF	NA	0.48	0.48	0.48
PCB 174	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	**Measured Conc. (ng)**	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA

	Species	YLPR	YLPR	YLPR	YLPR LIV
	Sample ID	YLPR EB A	YLPR EB B	YLPR WB	215YLPRL
PCB 45	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 91	Measured Conc. (ng)	ND	ND	0.04	ND
	Concenration (ng/g)	ND	ND	0.04	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	0.03	ND
	EF	NA	NA	0.42	NA
PCB 95	Measured Conc. (ng)	0.09	ND	0.10	0.47
	Concenration (ng/g)	0.09	ND	0.11	0.55
	Lipid Normalized Concentration (ng/g_{lipid})	0.03	ND	0.07	0.09
	EF	0.54	NA	0.50	0.52
PCB 136	Measured Conc. (ng)	ND	0.12	ND	ND
	Concenration (ng/g)	ND	0.12	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	0.04	ND	ND
	EF	NA	0.32	NA	NA
PCB 149	Measured Conc. (ng)	0.31	0.31	0.20	ND
	Concenration (ng/g)	0.31	0.32	0.21	ND
	Lipid Normalized Concentration (ng/g_{lipid})	0.11	0.11	0.13	ND
	EF	0.49	0.49	0.44	NA
PCB 174	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA
PCB 183	Measured Conc. (ng)	ND	ND	ND	ND
	Concenration (ng/g)	ND	ND	ND	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND	ND	ND	ND
	EF	NA	NA	NA	NA

	Species Sample ID	YLPR LIV YLPRLIV
PCB 45	Measured Conc. (ng)	ND
	Concenration (ng/g)	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND
	EF	NA
PCB 91	Measured Conc. (ng)	0.45
	Concenration (ng/g)	0.26
	Lipid Normalized Concentration (ng/g_{lipid})	0.12
	EF	0.52
PCB 95	Measured Conc. (ng)	2.08
	Concenration (ng/g)	1.22
	Lipid Normalized Concentration (ng/g_{lipid})	0.53
	EF	0.51
PCB 136	Measured Conc. (ng)	0.68
	Concenration (ng/g)	0.40
	Lipid Normalized Concentration (ng/g_{lipid})	0.10
	EF	0.49
PCB 149	Measured Conc. (ng)	4.36
	Concenration (ng/g)	2.54
	Lipid Normalized Concentration (ng/g_{lipid})	1.11
	EF	0.50
PCB 174	Measured Conc. (ng)	ND
	Concenration (ng/g)	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND
	EF	NA
PCB 183	Measured Conc. (ng)	ND
	Concenration (ng/g)	ND
	Lipid Normalized Concentration (ng/g_{lipid})	ND
	EF	NA

Appendix 3 - Total PCB Analysis Raw Data

Sample ID	**tbylpr**	**ebylpr**	**wbylpr**	**mayylpr**
Total CB (ng/g_{lipid})	497.33	481.57	295.76	993.62
%mono	0.00%	0.00%	0.00%	0.00%
%di	18.88%	30.32%	7.54%	13.27%
%tri	5.59%	19.52%	9.59%	3.78%
%tetra	16.56%	15.32%	17.83%	4.15%
%penta	18.68%	9.86%	20.04%	6.19%
%hexa	12.69%	10.97%	17.62%	10.41%
%hepta	8.77%	5.81%	6.83%	16.41%
%octa	3.68%	5.04%	10.59%	29.71%
%nona	3.77%	3.16%	3.15%	16.08%
%deca	11.38%	0.00%	6.83%	0.00%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
5	2.70	0.00	3.15	24.50
6	34.65	6.86	0.00	56.62
7	0.00	5.02	0.00	0.00
8	2.86	14.38	10.52	0.00
9	10.32	10.25	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00
13/27	0.00	0.00	0.00	0.00
14	7.83	15.18	8.63	8.20
15	35.54	94.34	0.00	42.49
16	2.02	0.00	0.00	0.00
17	1.58	21.18	0.00	0.00
18	4.00	14.14	5.72	4.31
19	0.00	0.00	0.00	8.04
20/33	2.16	12.80	3.27	3.73
22	1.36	6.83	2.63	0.00
24	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	2.39
26	0.00	0.00	0.00	0.00
28	4.64	8.17	6.87	4.60
29	8.46	14.17	9.46	14.50
30	0.00	0.00	0.00	0.00
31/53	0.00	0.00	0.00	0.00
32	1.38	0.00	0.00	0.00
34/54	3.97	0.00	0.00	0.00
35	0.00	16.68	0.00	0.00
37/40/103	0.69	0.00	1.22	0.00
41	0.00	0.00	1.14	0.00
42/59	1.70	3.11	1.58	1.71
44	5.16	24.02	8.29	7.06
45	0.47	0.00	0.00	0.00
46	0.00	0.00	0.61	0.00

Sample ID	tbylpr	ebylpr	wbylpr	mayylpr
Congener				
47/104	0.00	0.00	1.34	0.00
48	0.00	0.00	0.00	0.00
49	2.81	0.00	3.55	3.62
51	0.00	4.24	0.00	0.00
52	4.60	0.00	8.21	11.57
53	3.09	11.02	5.80	0.00
56/84	1.29	1.11	2.55	2.39
60/90/101	3.47	0.00	3.88	5.02
63/93	0.00	0.00	0.00	0.00
64	1.21	0.00	2.90	2.61
67	0.00	0.00	0.00	0.00
68/91	91.73	34.01	4.98	3.34
69	0.00	0.00	0.00	0.00
70	6.46	5.91	8.15	4.57
71	1.30	0.00	2.42	2.75
73	0.00	0.00	0.00	0.00
74	3.97	0.00	3.76	2.80
75	1.19	7.92	0.00	0.00
77/144	0.00	0.00	0.36	0.00
81	0.56	0.00	0.00	0.00
82/151	0.00	0.00	0.00	0.00
83/119	0.00	0.00	0.00	0.00
85/154	0.60	0.00	1.22	0.97
87	2.28	0.00	6.80	2.89
92	0.00	0.00	0.00	0.00
95	3.54	6.61	3.56	3.67
97	1.08	0.00	5.47	1.77
99	4.06	2.10	4.86	4.87
100	0.00	0.00	0.00	0.00
105/141	3.63	2.93	4.76	2.18
108/123	0.00	0.00	0.00	0.00
110	5.49	0.00	6.50	6.60
114	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	25.28	19.75	21.66	33.88
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	0.00	0.00	0.00	0.00
128/185	0.00	0.00	0.00	0.00
129/178	0.00	0.00	0.00	0.00
130	0.00	0.00	0.00	0.00
131	12.35	10.97	11.82	12.73
134	0.00	0.00	0.00	0.00
135	0.00	0.00	0.00	0.00
136	0.00	0.00	0.00	0.00
137	0.00	7.28	6.08	0.00
138	13.36	14.95	11.43	27.75
146	5.13	0.00	0.00	3.54
147	0.00	0.00	0.00	0.00
149	6.11	9.80	3.28	6.01
153	7.35	8.38	5.21	8.67
156	0.00	0.00	0.00	0.00
157	15.47	0.00	11.13	36.70
158	1.25	0.00	0.00	6.47
159	1847.06	1539.41	1988.07	2853.88
163	0.00	0.00	0.00	0.00

Sample ID	**tbylpr**	**ebylpr**	**wbylpr**	**mayylpr**
Congener				
164	0.00	0.00	0.00	0.00
166	336.75	264.69	363.27	525.99
167	0.00	0.00	0.00	0.00
170	1.88	0.00	3.96	64.63
172	0.00	0.00	0.00	0.00
173	0.00	0.00	0.00	0.00
174	11.65	0.00	0.00	29.88
175	0.83	0.00	0.00	0.00
176	0.00	0.00	0.00	0.00
177	10.05	0.00	0.00	12.96
179	2.29	0.00	0.00	2.08
180	7.60	14.86	10.35	21.15
183/187	5.19	13.09	3.51	13.65
189	4.11	0.00	0.00	0.00
190	0.00	0.00	0.00	0.00
191	0.00	0.00	2.37	18.71
193	0.00	0.00	0.00	0.00
194	3.43	0.00	15.63	88.60
195/207	2.45	30.45	7.58	0.00
196/203	5.05	0.00	1.66	11.75
197	0.00	0.00	0.00	0.00
199	2.60	9.06	4.13	52.01
200	0.00	0.00	0.00	0.00
202	0.00	0.00	0.00	0.00
204	0.00	0.00	0.00	0.00
205	5.97	0.00	6.11	142.89
206	17.51	0.00	5.51	159.81
208	0.00	0.00	0.00	0.00
209	56.59	0.00	20.20	0.00

Sample ID	**215YLPR**	**YLPR EB A**	**YLPR EB B**	**YLPR WB**
Total CB (ng/g$_{lipid}$)	293.36	200.07	178.80	329.87
%mono	0.00%	0.00%	0.00%	0.00%
%di	25.22%	20.21%	18.61%	21.73%
%tri	18.11%	14.12%	12.87%	13.21%
%tetra	26.19%	8.61%	13.61%	18.40%
%penta	12.04%	14.20%	20.81%	19.72%
%hexa	6.22%	11.82%	22.42%	13.44%
%hepta	9.15%	14.98%	7.85%	10.38%
%octa	1.97%	8.67%	2.12%	1.65%
%nona	1.10%	7.38%	0.82%	1.01%
%deca	0.00%	0.00%	0.89%	0.46%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00
6	61.79	9.43	4.07	16.58
7	0.00	0.00	1.02	2.48
8	0.00	2.57	6.96	6.15
9	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	1.55	0.00
13/27	0.00	0.00	0.47	0.00
14	12.21	6.44	2.16	14.71
15	0.00	22.00	17.26	31.77
16	7.56	0.00	0.00	0.00
17	7.41	4.01	1.31	3.36
18	0.00	0.00	0.00	0.00
19	28.59	6.73	2.37	5.13
20/33	0.00	2.03	2.15	0.00
22	0.00	0.00	2.50	4.01
24	0.00	2.12	0.00	3.00
25	0.00	2.30	2.26	4.49
26	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00
29	0.00	4.26	5.24	13.01
30	0.00	84.13	72.74	175.23
31/53	0.00	3.16	3.04	6.29
32	5.18	4.20	3.93	5.38
34/54	5.56	1.52	2.37	2.69
35	0.00	0.00	0.00	0.00
37/40/103	4.85	0.86	0.96	2.12
41	0.00	0.00	1.38	0.00
42/59	0.00	0.80	1.07	2.22
44	9.34	2.90	4.08	7.48
45	0.00	0.00	0.00	0.00
46	0.00	0.00	0.00	3.43
47/104	0.00	0.00	0.00	0.00
48	0.00	0.00	0.00	1.85
49	3.52	1.28	1.40	2.70
51	0.00	0.00	0.00	0.00

Sample ID	215YLPR	YLPR EB A	YLPR EB B	YLPR WB
Congener				
52	0.00	0.00	0.00	0.00
53	5.97	0.00	0.00	0.00
56/84	2.23	0.71	0.85	2.26
60/90/101	4.49	0.73	0.89	3.49
63/93	0.00	0.00	0.00	0.00
64	0.00	0.84	1.70	4.05
67	0.00	0.00	0.75	1.33
68/91	11.29	1.54	2.69	4.78
69	7.73	0.00	0.00	0.00
70	0.00	2.02	2.36	4.05
71	0.00	1.11	1.49	3.04
73	25.22	1.28	0.00	1.89
74	5.20	1.47	1.78	3.44
75	0.00	0.00	1.13	3.54
77/144	0.00	0.44	0.00	0.00
81	7.19	1.33	2.10	11.80
82/151	1.54	0.74	0.79	1.80
83/119	0.00	0.32	0.00	0.00
85/154	0.00	0.00	0.00	0.00
87	0.00	1.19	0.79	2.57
92	0.00	0.00	0.00	0.00
95	0.00	1.86	2.11	4.80
97	0.00	0.80	0.87	4.56
99	4.78	3.22	2.98	11.35
100	0.00	0.00	0.00	1.54
105/141	1.05	0.73	0.63	1.55
108/123	0.00	0.00	0.00	0.00
110	0.00	2.67	1.85	0.00
114	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	15.86	14.17	17.00	27.88
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	2.02	1.56	8.23	4.13
128/185	0.00	0.00	0.00	0.00
129/178	0.00	0.00	0.00	0.00
130	0.00	0.75	0.29	0.00
131	4.56	1.61	1.89	4.00
134	0.00	0.00	0.00	0.00
135	1.40	1.05	1.78	3.43
136	0.00	0.00	0.00	0.00
137	0.00	0.58	0.39	0.00
138	4.65	5.70	5.73	9.78
146	0.00	4.49	2.75	8.72
147	0.00	0.00	0.00	0.00
149	3.04	2.93	1.89	7.22
153	3.30	3.48	3.34	6.53
156	0.00	0.00	0.00	0.00
157	0.00	0.00	0.00	0.00
158	0.00	0.78	0.92	1.10
159	9650.65	1306.51	1384.28	2345.22
163	0.00	0.00	0.00	0.00
164	0.00	1.32	20.39	1.88
166	40.35	145.21	175.41	280.08
167	0.00	0.00	0.00	0.00
170	0.00	2.67	0.73	1.94

Sample ID Congener	215YLPR	YLPR EB A	YLPR EB B	YLPR WB
172	10.91	0.00	0.00	0.00
173	0.00	0.00	0.00	0.00
174	0.00	0.00	0.00	0.00
175	0.00	0.00	0.00	0.80
176	0.00	0.00	0.00	0.00
177	5.34	4.43	3.76	7.32
179	2.33	1.12	2.16	5.78
180	2.66	6.74	3.56	8.66
183/187	1.75	2.86	1.66	3.17
189	0.62	2.11	0.93	2.02
190	0.00	0.00	0.25	0.00
191	3.24	10.04	0.99	4.56
193	0.00	0.00	0.00	0.00
194	0.18	2.52	0.39	0.77
195/207	3.61	0.00	0.16	0.00
196/203	0.47	2.82	0.32	0.82
197	0.00	4.30	0.00	0.00
199	0.97	2.39	0.70	1.61
200	0.00	0.00	1.36	0.00
202	0.00	0.00	0.00	0.00
204	0.00	0.00	0.00	0.00
205	2.36	5.32	0.95	2.27
206	1.43	13.02	1.39	3.32
208	0.00	1.75	0.00	0.00
209	0.00	0.00	1.59	1.51

Sample ID	**215YLPRL**	**LIV COMP**	**WHSC060519**	**SPSH**
Total CB (ng/g$_{lipid}$)	261.23	459.98	118.89	193.86
%mono	0.00%	0.00%	0.00%	0.00%
%di	8.06%	17.17%	8.10%	4.98%
%tri	50.26%	9.36%	10.40%	9.05%
%tetra	21.24%	10.10%	9.46%	20.23%
%penta	6.77%	15.35%	8.86%	17.97%
%hexa	6.08%	9.72%	14.98%	15.50%
%hepta	5.12%	25.40%	23.02%	18.11%
%octa	1.58%	8.28%	13.49%	11.57%
%nona	0.89%	4.62%	9.51%	1.79%
%deca	0.00%	0.00%	2.19%	0.81%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00
6	15.79	28.02	7.24	3.71
7	4.02	0.00	0.00	0.00
8	0.00	11.56	2.38	0.00
9	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	1.11
12	0.00	0.00	0.00	0.00
13/27	1.27	0.00	0.00	0.00
14	0.61	21.23	0.00	0.00
15	0.00	18.19	0.00	4.83
16	4.67	5.59	0.00	0.00
17	6.57	6.84	1.12	0.00
18	0.00	0.00	0.00	0.00
19	0.67	5.75	4.43	0.00
20/33	0.00	5.08	0.00	0.75
22	6.64	0.00	0.00	0.00
24	0.55	3.92	0.00	0.66
25	0.00	3.32	0.00	0.00
26	2.97	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00
29	95.22	2.61	2.72	5.16
30	0.00	509.34	36.63	13.61
31/53	8.14	0.00	0.98	1.81
32	4.60	8.24	3.56	7.91
34/54	0.00	0.00	0.00	3.32
35	4.70	0.00	0.00	0.00
37/40/103	0.00	5.09	0.14	1.48
41	0.00	0.00	0.00	1.37
42/59	1.28	0.00	0.00	1.10
44	9.51	15.17	0.86	0.00
45	0.00	0.00	0.00	0.00
46	0.00	0.00	0.00	0.00
47/104	0.00	0.00	0.00	0.00
48	3.12	0.00	0.00	2.17
49	3.63	0.00	3.30	2.53
51	0.00	0.00	0.00	0.00

Sample ID	215YLPRL	LIV COMP	WHSC060519	SPSH
Congener				
52	0.00	0.00	0.00	0.00
53	12.60	7.31	0.76	0.00
56/84	1.81	0.00	0.00	1.77
60/90/101	2.24	3.08	0.41	1.90
63/93	0.00	0.00	0.00	0.00
64	2.21	7.37	0.00	2.80
67	0.00	4.97	0.00	0.00
68/91	2.89	4.54	3.43	5.61
69	5.80	0.00	0.00	0.00
70	0.00	0.00	0.23	8.84
71	0.00	0.00	0.00	2.94
73	5.42	0.00	0.00	0.00
74	3.36	6.63	0.27	4.68
75	0.00	0.00	0.00	0.67
77/144	0.96	0.00	0.00	1.00
81	0.91	0.00	3.44	4.22
82/151	1.50	1.64	0.36	1.20
83/119	0.00	0.00	0.00	0.00
85/154	0.72	0.00	0.14	0.90
87	0.00	3.91	0.31	1.95
92	0.00	0.00	0.00	0.00
95	3.17	0.00	0.44	3.04
97	0.00	4.70	0.00	2.13
99	2.17	7.09	0.66	3.66
100	0.00	3.94	0.00	0.00
105/141	3.63	1.18	0.47	1.24
108/123	0.00	0.00	0.08	0.00
110	0.00	6.01	0.00	5.83
114	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	5.58	33.57	4.34	8.91
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.74
124	0.00	3.94	0.39	1.85
128/185	0.00	0.00	3.60	0.00
129/178	0.00	0.00	0.00	0.00
130	0.00	0.00	0.00	0.00
131	3.19	5.20	0.98	2.88
134	0.00	0.00	0.00	0.00
135	1.35	1.37	0.00	1.71
136	0.00	0.00	0.00	0.00
137	0.00	3.47	0.00	0.00
138	3.31	0.00	2.25	5.90
146	0.00	7.99	1.73	6.52
147	0.00	0.00	0.00	0.00
149	2.53	9.75	0.78	3.31
153	2.10	7.56	1.24	3.43
156	0.00	0.00	2.72	0.00
157	0.00	0.00	2.85	0.00
158	0.00	5.40	0.00	0.86
159	965.07	4306.63	555.31	3154.57
163	0.00	0.00	0.00	0.00
164	0.00	2.57	0.00	2.92
166	23.36	595.82	14.75	355.32
167	0.00	0.00	2.97	0.00
170	0.00	10.04	0.36	0.00

Sample ID	215YLPRL	LIV COMP	WHSC060519	SPSH
Congener				
172	5.62	0.00	0.00	0.00
173	0.00	0.00	3.64	0.00
174	0.00	35.88	5.35	0.00
175	0.00	0.00	0.00	0.00
176	0.00	0.00	0.00	4.53
177	0.00	10.26	5.76	0.00
179	0.00	4.45	2.46	4.65
180	1.71	17.57	2.90	8.98
183/187	2.79	7.87	0.69	4.51
189	0.00	5.79	1.16	1.40
190	0.00	0.00	4.31	0.00
191	3.25	24.98	0.77	11.05
193	0.00	0.00	0.00	0.00
194	0.39	3.71	5.03	2.86
195/207	0.00	1.76	0.28	0.00
196/203	1.09	3.99	1.31	4.09
197	0.00	15.36	3.28	14.48
199	1.40	7.19	0.38	0.00
200	0.00	6.96	0.00	0.00
202	0.00	0.00	4.19	0.00
204	0.00	0.00	0.00	0.00
205	1.25	0.00	1.72	0.99
206	2.32	16.76	6.85	3.46
208	0.00	3.64	4.32	0.00
209	0.00	0.00	2.60	1.56

Sample ID	**WBCISC1**	**WBCISC2**	**179CISC**	**215CISC**
Total CB (ng/g_{lipid})	383.12	120.90	196.59	851.79
1	0.00%	0.00%	0.00%	0.00%
2	3.55%	9.55%	5.74%	11.21%
3	38.72%	42.65%	44.78%	62.47%
4	38.58%	31.47%	11.01%	5.43%
5	12.27%	8.95%	13.26%	10.31%
6	3.40%	3.01%	8.36%	4.88%
7	2.66%	3.15%	12.73%	4.53%
8	0.64%	0.91%	3.16%	0.69%
9	0.17%	0.31%	0.87%	0.47%
10	0.00%	0.00%	0.09%	0.00%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00
6	3.49	1.02	11.29	92.27
7	3.38	3.02	0.00	0.00
8	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00
13/27	3.59	1.15	0.00	0.00
14	4.94	2.86	0.00	3.25
15	0.00	4.08	0.00	0.00
16	13.08	3.61	0.76	4.22
17	23.97	6.18	0.51	0.00
18	0.00	0.00	0.00	0.00
19	3.78	1.51	4.33	1.98
20/33	0.00	0.00	0.00	0.00
22	18.34	4.71	1.64	0.00
24	2.17	0.79	0.00	0.00
25	5.99	1.92	0.69	0.00
26	8.02	2.10	0.00	0.00
28	0.00	0.00	0.00	0.00
29	24.99	19.57	75.49	523.38
30	0.00	0.00	0.00	0.00
31/53	18.60	4.26	0.70	0.00
32	18.14	3.88	0.51	2.55
34/54	0.00	0.36	0.68	0.00
35	17.15	4.03	2.85	0.00
37/40/103	4.88	1.19	1.67	0.00
41	6.26	1.24	0.00	0.00
42/59	5.65	1.22	0.75	0.00
44	22.28	5.08	2.49	0.00
45	0.00	0.00	0.00	0.00
46	5.07	1.38	1.11	0.00
47/104	0.00	0.00	0.00	0.00
48	9.42	2.40	1.35	0.00
49	12.43	3.03	0.73	21.62
51	3.90	1.03	0.00	0.00

Sample ID	WBCISC1	WBCISC2	179CISC	215CISC
Congener				
52	0.00	0.00	0.00	0.00
53	28.56	6.55	0.65	0.00
56/84	4.64	1.13	1.60	4.90
60/90/101	4.71	0.98	2.01	7.22
63/93	0.00	0.00	0.00	0.00
64	7.87	1.79	1.77	0.00
67	4.21	1.24	1.12	0.00
68/91	5.67	1.29	2.44	13.67
69	14.02	3.50	1.43	0.00
70	0.00	0.00	0.00	0.00
71	0.00	0.00	0.00	0.00
73	0.00	2.54	1.00	0.00
74	9.97	2.19	2.48	7.95
75	0.00	0.49	1.47	0.00
77/144	1.05	0.29	0.95	0.00
81	0.00	0.00	0.90	5.02
82/151	1.64	0.39	1.34	4.39
83/119	1.29	0.00	0.00	0.00
85/154	0.99	0.28	0.82	0.00
87	1.47	0.59	1.87	0.00
92	0.00	0.00	0.00	0.00
95	7.56	1.79	2.19	7.45
97	2.23	0.45	1.23	1.90
99	4.22	1.08	3.11	6.92
100	6.24	1.11	0.00	0.00
105/141	1.11	0.24	0.86	2.43
108/123	0.40	0.00	0.00	0.00
110	4.46	1.12	2.12	6.35
114	0.00	0.00	0.35	0.00
115	0.00	0.00	0.00	0.00
117	6.92	1.85	8.32	45.19
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	0.00	0.00	1.46	2.50
128/185	0.85	0.22	0.00	0.00
129/178	0.00	0.10	0.00	0.00
130	0.00	0.00	0.65	0.00
131	0.00	0.32	1.78	7.57
134	0.00	0.00	0.00	0.00
135	1.58	0.42	1.39	3.36
136	0.00	0.00	0.00	0.00
137	0.00	0.00	0.79	0.00
138	2.35	0.60	3.41	9.77
146	0.00	0.00	0.00	0.00
147	0.00	0.00	0.00	0.00
149	3.50	0.86	3.70	9.46
153	2.11	0.55	2.11	8.03
156	0.00	0.00	0.00	0.00
157	0.00	0.00	0.00	0.00
158	0.68	0.15	0.64	0.00
159	236.18	62.42	1586.29	9460.74
163	0.00	0.00	0.00	0.00
164	0.00	0.00	0.00	0.00
166	9.05	2.44	14.43	91.78
167	0.00	0.00	0.00	0.00
170	0.00	0.00	0.00	0.00

Sample ID **Congener**	WBCISC1	WBCISC2	179CISC	215CISC
172	1.98	1.44	11.31	14.67
173	0.00	0.00	0.00	0.00
174	1.82	0.51	5.09	0.00
175	0.00	0.00	0.00	0.00
176	0.00	0.00	0.00	0.00
177	0.78	0.22	1.81	6.25
179	1.03	0.28	0.77	2.27
180	1.16	0.28	1.70	4.26
183/187	1.83	0.39	1.49	5.26
189	0.00	0.00	0.41	0.91
190	0.00	0.13	0.00	0.00
191	1.58	0.53	2.46	4.96
193	0.00	0.00	0.00	0.00
194	0.13	0.02	0.14	0.41
195/207	0.80	0.23	1.67	1.41
196/203	0.23	0.15	1.52	0.79
197	0.00	0.16	0.00	0.00
199	0.20	0.19	1.09	1.60
200	0.65	0.23	0.00	0.00
202	0.86	0.24	2.20	0.00
204	0.00	0.00	0.00	0.00
205	0.00	0.00	0.42	2.41
206	0.14	0.26	0.63	3.27
208	0.11	0.00	0.24	0.00
209	0.00	0.00	0.17	0.00

Sample ID	**CISCLIV1**	**CISCLIV2**	**179CISCL**	**215CISCL**
Total CB (ng/g_{lipid})	211.03	995.37	440.30	728.32
1	2.70%	2.16%	0.00%	0.00%
2	9.06%	2.38%	12.08%	13.66%
3	41.72%	46.57%	60.44%	63.23%
4	31.57%	37.49%	20.40%	12.44%
5	9.29%	11.73%	4.75%	4.66%
6	2.73%	3.52%	1.26%	2.58%
7	2.62%	0.87%	0.94%	2.71%
8	0.30%	0.00%	0.05%	0.32%
9	0.00%	0.00%	0.07%	0.36%
10	0.00%	0.00%	0.00%	0.04%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	5.70	20.51	0.00	0.00
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00
6	1.63	7.30	21.69	54.84
7	4.63	7.78	13.04	0.00
8	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00
10	0.89	3.10	0.00	0.00
12	0.00	0.00	0.00	0.00
13/27	1.74	8.92	0.00	2.82
14	3.54	0.00	8.48	43.27
15	7.57	0.00	9.97	0.00
16	5.91	26.70	10.31	6.77
17	10.22	56.97	18.21	44.92
18	0.00	0.00	0.00	0.00
19	1.95	8.36	12.70	2.01
20/33	0.00	0.00	0.00	0.00
22	8.43	43.93	11.02	0.00
24	1.14	0.00	0.00	0.00
25	2.77	15.81	4.34	3.42
26	3.53	18.93	5.64	0.00
28	0.00	0.00	0.00	0.00
29	34.52	174.95	185.96	390.44
30	0.00	0.00	0.00	0.00
31/53	7.61	41.34	14.20	4.60
32	6.48	26.31	10.27	5.09
34/54	0.55	3.07	1.15	5.24
35	7.42	40.08	0.00	0.00
37/40/103	2.22	12.00	0.00	4.60
41	2.86	15.42	0.00	0.00
42/59	2.48	13.68	1.98	0.00
44	9.57	49.90	10.68	8.96
45	0.00	0.00	0.00	0.00
46	2.36	12.63	0.00	0.00
47/104	0.00	0.00	0.00	0.00
48	4.03	22.51	5.01	0.00
49	5.33	29.71	5.61	22.82
51	1.82	9.62	0.00	0.00

Sample ID Congener	CISCLIV1	CISCLIV2	179CISCL	215CISCL
52	0.00	0.00	0.00	0.00
53	11.71	66.06	20.89	5.50
56/84	2.04	10.91	2.45	0.00
60/90/101	1.95	10.86	2.65	3.96
63/93	0.00	0.00	0.00	0.00
64	3.33	17.95	3.60	3.10
67	2.61	11.67	5.87	0.00
68/91	2.40	13.39	4.83	9.63
69	6.00	31.62	9.11	7.33
70	0.00	0.00	0.00	0.00
71	0.00	0.00	0.00	0.00
73	2.60	10.28	7.52	24.00
74	3.99	21.74	5.84	0.00
75	0.00	0.00	0.46	0.00
77/144	0.51	3.13	0.18	0.00
81	0.00	0.00	0.96	6.32
82/151	0.66	3.89	0.76	1.29
83/119	0.66	4.08	0.00	0.00
85/154	0.43	2.60	0.00	0.34
87	0.73	3.63	0.00	0.00
92	0.00	0.00	0.00	0.00
95	3.01	16.38	5.22	0.00
97	1.06	6.33	0.00	0.00
99	1.75	10.64	1.80	4.14
100	2.42	16.87	0.00	0.00
105/141	0.42	2.65	2.85	9.59
108/123	0.20	0.00	0.00	0.00
110	2.32	13.61	1.60	0.00
114	0.09	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	1.67	11.99	4.87	13.52
118	0.00	0.00	0.00	0.00
122/165	0.15	0.00	0.00	0.00
124	0.45	0.00	0.22	1.67
128/185	0.34	0.00	0.00	0.00
129/178	0.15	0.96	0.00	0.00
130	0.00	0.00	0.00	0.00
131	0.00	0.00	1.36	4.01
134	0.00	0.00	0.00	0.00
135	0.71	4.27	0.00	0.00
136	0.00	0.00	0.00	0.00
137	0.26	0.00	0.00	0.00
138	0.69	4.44	0.00	3.95
146	0.00	0.00	0.00	0.00
147	0.00	0.00	0.00	0.00
149	1.43	8.77	1.42	2.41
153	0.83	5.22	0.87	2.83
156	0.00	0.00	0.00	0.00
157	0.00	0.00	0.00	0.00
158	0.23	2.32	0.00	0.00
159	109.65	0.00	1033.06	9090.91
163	0.00	0.00	0.00	0.00
164	0.28	1.84	0.00	0.00
166	3.97	0.00	23.88	36.75
167	0.00	0.00	0.00	0.00
170	0.00	0.00	0.00	0.00

Sample ID	CISCLIV1	CISCLIV2	179CISCL	215CISCL
Congener				
172	2.70	0.00	2.03	10.33
173	0.00	0.00	0.00	0.00
174	0.84	0.00	0.00	0.00
175	0.00	0.00	0.00	0.00
176	0.00	0.00	0.00	0.00
177	0.36	0.00	0.00	0.00
179	0.37	2.90	0.30	1.97
180	0.46	0.00	0.50	2.40
183/187	0.73	4.89	0.59	1.49
189	0.00	0.00	0.10	0.63
190	0.00	0.00	0.00	0.00
191	0.00	0.00	0.65	2.94
193	0.00	0.00	0.00	0.00
194	0.00	0.00	0.04	0.18
195/207	0.00	0.00	0.00	0.92
196/203	0.00	0.00	0.10	0.38
197	0.24	0.00	0.00	0.00
199	0.00	0.00	0.00	0.83
200	0.00	0.00	0.00	0.00
202	0.40	0.00	0.00	0.00
204	0.00	0.00	0.00	0.00
205	0.00	0.00	0.08	0.45
206	0.00	0.00	0.31	2.17
208	0.00	0.00	0.00	0.00
209	0.00	0.00	0.00	0.26

Sample ID	**LKWHA**	**LKWHB**	**LKWHC**	**LKWH434L**	**LKWH492L**
Total CB (ng/g$_{lipid}$)	329.55	148.37	181.38	160.24	412.10
1	0.00%	0.00%	0.00%	0.00%	0.00%
2	4.94%	9.23%	7.77%	3.84%	6.16%
3	11.60%	27.82%	3.88%	8.63%	11.80%
4	35.26%	24.80%	17.43%	11.58%	14.06%
5	15.59%	14.68%	15.58%	32.11%	11.05%
6	10.84%	8.67%	13.15%	21.15%	5.93%
7	17.75%	9.69%	27.17%	14.57%	21.64%
8	3.16%	3.37%	7.58%	6.94%	18.52%
9	0.83%	1.36%	4.31%	1.16%	5.99%
10	0.03%	0.39%	3.12%	0.00%	4.84%
	100.00%	100.00%	100.00%	100.00%	100.00%
Congener					
1	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00
6	4.48	7.00	9.40	2.21	0.86
7	6.16	0.00	0.00	0.00	3.16
8	5.64	5.47	2.76	1.64	3.45
9	0.00	0.00	0.00	0.00	0.00
10	0.00	0.00	1.94	0.00	0.00
12	0.00	0.00	0.00	0.00	3.64
13/27	0.00	2.46	0.00	0.00	2.06
14	0.00	0.00	0.00	2.30	13.25
15	0.00	0.00	0.00	0.00	0.00
16	0.00	5.66	0.65	1.79	5.43
17	0.00	8.17	0.34	2.24	4.29
18	0.00	0.00	0.00	0.00	0.00
19	0.00	2.70	0.00	2.50	3.91
20/33	0.00	0.00	0.00	0.00	0.00
22	5.60	1.95	0.54	1.00	5.05
24	0.00	0.00	0.00	0.00	3.84
25	7.01	0.00	0.00	0.65	5.25
26	0.00	4.91	0.00	1.20	3.02
28	0.00	0.00	0.00	0.00	0.00
29	7.14	5.86	2.82	1.15	6.11
30	55.00	56.91	14.11	37.79	93.39
31/53	3.62	2.63	1.05	1.38	6.39
32	10.99	4.60	0.94	1.35	5.71
34/54	5.81	0.00	2.15	0.00	2.09
35	0.00	4.09	0.00	1.03	0.00
37/40/103	8.38	2.34	0.46	0.67	2.32
41	0.00	0.00	0.54	0.63	0.00
42/59	5.19	0.96	0.69	0.35	2.52
44	36.06	7.17	3.93	2.16	8.60
45	0.00	2.08	0.59	1.26	3.06
46	2.09	0.00	0.00	0.00	2.50
47/104	0.00	0.00	0.00	0.00	0.00
48	4.13	2.36	1.08	0.91	2.98
49	3.72	2.42	1.49	1.38	4.82
51	7.13	0.66	0.00	0.00	2.73
52	0.00	0.00	0.00	0.00	0.00
53	3.81	0.00	0.00	0.00	0.00
56/84	3.22	1.15	0.87	0.72	2.57

Sample ID	LKWHA	LKWHB	LKWHC	LKWH434L	LKWH492L
Congener					
60/90/101	3.76	1.43	0.99	0.96	2.96
63/93	0.00	0.00	0.00	0.00	0.00
64	0.00	1.98	1.09	0.68	2.52
67	12.18	0.00	1.86	0.00	0.00
68/91	5.07	1.83	3.49	0.95	2.97
69	6.92	4.77	2.38	1.90	3.07
70	6.41	3.16	3.06	1.43	5.02
71	0.00	2.36	0.95	0.67	0.00
73	4.04	0.00	0.00	0.00	0.00
74	4.38	2.24	1.74	1.32	3.70
75	0.00	1.61	0.90	0.68	0.00
77/144	0.00	0.35	0.47	1.36	3.65
81	7.25	0.80	6.84	2.44	5.84
82/151	1.98	1.01	1.57	0.73	0.00
83/119	0.00	0.40	0.00	0.00	0.00
85/154	1.30	0.00	0.51	0.00	0.00
87	2.69	1.01	1.28	1.43	0.00
92	0.00	0.00	0.00	0.00	0.00
95	5.59	2.66	2.49	1.46	4.05
97	0.00	1.85	0.59	1.01	0.00
99	8.88	2.77	2.08	3.56	7.32
100	0.00	0.00	0.00	0.32	0.00
105/141	1.59	0.38	1.31	1.05	0.41
108/123	0.00	0.00	0.15	0.79	0.00
110	4.11	2.48	2.43	3.61	9.24
114	0.00	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00	0.00
117	16.84	5.55	13.72	35.61	19.23
118	0.00	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00	0.00
124	1.36	1.13	0.83	1.07	0.00
128/185	0.00	0.00	0.00	0.00	0.00
129/178	0.00	0.00	0.32	0.00	0.00
130	0.00	0.00	0.30	1.26	0.00
131	2.95	1.21	1.30	0.00	1.71
134	0.00	0.00	0.00	0.00	0.00
135	2.06	0.68	1.01	1.16	0.00
136	0.00	0.00	0.00	0.00	0.00
137	0.66	0.00	0.63	0.73	0.00
138	11.66	2.69	5.55	8.37	4.44
146	4.48	1.99	3.07	5.98	0.00
147	0.00	0.00	0.00	0.00	0.00
149	5.60	3.15	4.51	3.44	9.07
153	5.89	2.11	4.68	5.37	2.03
156	0.00	0.00	0.00	0.00	0.00
157	0.00	0.00	0.00	1.78	0.00
158	0.00	0.16	0.64	1.44	5.16
159	1740.98	1142.29	1139.96	342.09	1915.71
163	0.00	0.00	0.00	0.00	0.00
164	0.00	0.00	0.07	1.17	0.00
166	205.78	94.28	157.32	56.29	265.29
167	0.00	0.00	0.00	1.64	0.00
170	2.44	1.37	1.74	2.22	20.50
172	0.00	0.00	0.00	0.00	0.00
173	0.00	0.00	0.00	0.60	0.00
174	12.63	0.00	12.50	1.74	0.00
175	0.41	0.00	0.20	1.29	0.00
176	0.00	0.38	0.00	0.00	0.00
177	16.31	0.00	6.49	1.84	0.00
179	6.60	1.81	7.00	0.99	0.00

Sample ID	LKWHA	LKWHB	LKWHC	LKWH434L	LKWH492L
Congener					
180	8.36	3.63	7.82	8.17	30.73
183/187	4.90	1.96	4.95	3.78	5.00
189	2.06	0.74	2.33	0.00	5.92
190	0.74	1.39	0.00	1.79	0.00
191	4.07	3.10	6.09	1.53	27.05
193	0.00	0.00	0.00	0.00	0.00
194	1.11	0.23	1.55	2.14	8.67
195/207	0.25	0.23	0.76	0.68	7.02
196/203	1.50	1.21	0.98	1.30	21.59
197	5.96	0.00	0.00	2.29	16.15
199	1.71	1.54	1.77	1.66	0.00
200	0.00	1.91	1.31	0.00	0.00
202	0.00	0.00	6.94	2.34	0.00
204	0.00	0.00	0.00	0.00	0.00
205	0.00	0.00	0.82	1.06	26.40
206	2.33	1.47	7.44	0.00	21.16
208	0.28	0.44	0.00	1.52	0.00
209	0.10	0.57	5.67	0.00	19.95

Sample ID	**WALL485-2**	**WALL540**	**WLIV485-2**	**WLIV 540**
Total CB (ng/g$_{lipid}$)	754.92	1108.81	207.92	1249.97
1	0.00%	0.00%	0.00%	0.00%
2	10.90%	6.40%	3.43%	1.33%
3	15.46%	16.79%	4.77%	4.94%
4	17.40%	13.86%	12.82%	10.08%
5	11.19%	10.07%	25.17%	19.36%
6	7.11%	9.13%	20.47%	19.41%
7	22.60%	27.68%	22.71%	22.71%
8	10.96%	9.63%	9.13%	14.26%
9	4.16%	4.41%	1.28%	5.87%
10	0.21%	2.03%	0.21%	2.04%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00
6	17.94	4.97	2.17	0.93
7	0.00	0.00	0.00	0.00
8	22.18	31.98	2.77	15.68
9	0.00	0.00	0.00	0.00
10	0.00	0.00	0.08	0.00
12	0.00	0.00	0.00	0.00
13/27	0.00	0.00	0.00	0.00
14	42.13	34.03	2.12	0.00
15	0.00	0.00	0.00	0.00
16	9.86	17.63	0.92	0.00
17	18.46	30.56	0.79	0.00
18	0.00	0.00	0.00	0.00
19	17.00	13.00	0.90	0.00
20/33	0.00	12.94	1.68	3.93
22	8.05	11.00	2.49	4.01
24	0.00	10.65	0.00	0.00
25	6.56	13.01	0.68	0.00
26	4.17	8.98	0.76	0.00
28	0.00	0.00	0.00	0.00
29	45.16	41.20	0.58	5.97
30	502.31	796.23	28.95	320.43
31/53	0.00	12.11	0.00	0.00
32	7.45	13.80	0.65	46.77
34/54	0.00	6.73	0.32	0.00
35	0.00	0.00	0.00	0.00
37/40/103	0.00	11.96	0.98	3.23
41	7.99	0.00	0.84	0.00
42/59	4.66	0.00	0.84	1.26
44	25.07	32.90	4.24	7.14
45	0.00	7.89	0.00	0.00
46	0.00	0.00	0.00	0.00
47/104	0.00	0.00	0.00	0.00
48	0.00	0.00	1.07	0.00
49	9.43	9.23	1.71	30.63
51	0.00	3.02	0.00	0.00

Sample ID	WALL485-2	WALL540	WLIV485-2	WLIV 540
Congener				
52	0.00	0.00	0.00	0.00
53	15.22	0.00	2.92	8.50
56/84	3.94	1.29	1.40	2.94
60/90/101	5.34	2.26	2.73	12.16
63/93	0.00	0.00	0.00	0.00
64	12.23	0.00	1.53	2.49
67	13.75	23.95	0.00	0.28
68/91	4.25	5.38	2.49	14.34
69	0.00	0.00	0.00	0.00
70	11.59	8.01	3.61	7.07
71	9.08	0.00	1.33	0.00
73	0.00	0.00	0.00	11.96
74	0.00	7.52	2.26	6.00
75	8.13	12.15	0.00	0.00
77/144	0.00	2.34	1.10	6.06
81	8.38	30.31	2.43	33.84
82/151	4.20	0.00	2.39	11.72
83/119	0.00	0.00	0.48	0.00
85/154	0.00	0.00	0.00	0.00
87	2.90	2.62	2.13	11.86
92	0.00	0.00	0.00	0.00
95	10.35	0.00	2.15	9.41
97	0.00	3.64	1.52	0.00
99	7.60	5.23	4.49	20.64
100	5.65	5.84	0.00	0.53
105/141	1.52	4.18	1.74	9.47
108/123	0.00	0.00	0.50	0.00
110	4.33	0.00	6.48	18.13
114	2.95	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	34.38	72.15	26.72	137.71
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	5.81	11.25	1.71	15.35
128/185	0.00	0.00	0.00	0.00
129/178	0.00	0.00	0.00	0.00
130	0.00	0.00	0.25	0.00
131	7.04	11.11	2.06	18.21
134	0.00	0.00	0.00	0.00
135	2.43	0.00	2.51	14.55
136	0.00	0.00	0.00	0.00
137	3.40	0.00	0.49	3.11
138	0.00	30.71	10.76	55.11
146	0.00	20.92	8.22	56.45
147	0.00	0.00	0.00	0.00
149	17.60	18.19	7.84	42.75
153	9.48	17.00	6.62	38.80
156	0.00	0.00	0.00	0.00
157	8.82	0.00	0.00	0.00
158	2.08	0.00	0.94	0.00
159	5896.23	5714.29	1265.18	11967.45
163	0.00	0.00	0.00	0.00
164	0.00	0.00	0.25	0.00
166	719.62	1081.25	203.30	1183.49
167	0.00	0.00	0.00	0.00
170	17.67	37.68	2.19	6.53

Sample ID **Congener**	**WALL485-2**	**WALL540**	**WLIV485-2**	**WLIV 540**
172	0.00	0.00	0.00	0.00
173	0.00	0.00	0.00	0.00
174	38.68	107.85	10.39	96.19
175	0.00	0.00	1.01	0.00
176	0.00	0.00	4.87	0.00
177	14.58	0.00	5.58	48.39
179	7.60	18.19	5.90	17.20
180	35.31	46.74	7.05	42.21
183/187	15.00	13.67	6.96	34.87
189	14.05	28.14	1.28	12.58
190	0.00	0.00	1.17	0.00
191	27.71	54.67	0.84	25.90
193	0.00	0.00	0.00	0.00
194	13.87	20.01	0.92	9.12
195/207	0.00	0.00	0.63	3.91
196/203	6.17	0.00	1.91	4.48
197	35.34	0.00	4.70	52.18
199	0.00	0.00	2.51	9.21
200	0.00	25.67	1.77	9.97
202	22.41	0.00	5.95	56.97
204	0.00	0.00	0.00	0.00
205	4.99	61.11	0.92	34.40
206	15.07	48.93	1.78	70.33
208	16.38	0.00	0.57	1.04
209	1.57	22.51	0.43	25.55

Sample ID	**NRPK A**	**NRPK B**	**NRPK C**	**NRPK 584**
Total CB ($\text{ng/g}_{\text{lipid}}$)	471.41	281.66	338.25	851.36
%mono	0.00%	0.00%	0.00%	0.00%
%di	7.18%	8.52%	9.21%	1.16%
%tri	18.55%	28.25%	21.66%	2.79%
%tetra	36.61%	29.20%	32.78%	9.96%
%penta	7.49%	7.91%	7.85%	12.93%
%hexa	5.64%	5.15%	4.21%	15.70%
%hepta	15.47%	14.09%	14.39%	31.58%
%octa	4.47%	3.01%	5.29%	7.56%
%nona	4.59%	3.87%	4.51%	9.82%
%deca	0.00%	0.00%	0.10%	8.49%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	3.62	1.22	1.61	0.00
5	0.00	0.00	0.00	0.00
6	4.05	2.51	3.05	2.92
7	2.44	0.00	0.00	0.00
8	18.62	19.24	22.50	0.00
9	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00
13/27	2.94	2.07	2.38	0.00
14	3.65	0.00	2.80	6.98
15	0.00	0.00	0.00	0.00
16	16.86	10.31	12.50	0.00
17	0.00	22.57	0.00	0.79
18	0.00	0.00	0.00	0.00
19	3.41	2.02	2.47	0.00
20/33	0.00	0.00	0.00	0.00
22	14.89	11.13	14.69	4.63
24	1.44	0.78	1.03	1.77
25	4.00	2.93	3.91	2.22
26	6.29	4.55	5.85	1.42
28	0.00	0.00	0.00	0.00
29	5.04	3.16	3.99	3.11
30	31.40	23.82	23.76	7.86
31/53	14.41	10.93	14.33	7.97
32	24.67	14.11	16.74	3.72
34/54	1.59	1.46	1.67	1.90
35	0.00	0.00	1.85	0.00
37/40/103	4.10	2.37	3.15	3.44
41	6.05	2.83	3.70	2.65
42/59	5.68	2.42	3.20	2.39
44	18.42	10.12	13.27	12.38
45	4.96	3.63	4.42	1.51
46	3.47	2.39	2.95	0.00
47/104	0.00	0.00	0.00	0.00
48	8.93	4.30	5.86	3.82
49	11.20	5.46	7.55	5.71
51	1.09	0.00	0.00	0.00

Sample ID	NRPK A	NRPK B	NRPK C	NRPK 584
Congener				
52	0.00	0.00	0.00	0.00
53	23.40	18.20	24.42	0.00
56/84	2.95	1.76	2.38	4.84
60/90/101	3.20	1.96	2.71	6.91
63/93	0.00	0.00	0.00	0.00
64	5.12	3.24	4.35	4.62
67	3.41	1.44	1.85	0.39
68/91	5.28	3.74	4.79	6.43
69	13.19	0.70	1.08	0.00
70	12.41	7.56	10.58	16.19
71	6.66	3.33	4.46	3.74
73	23.71	1.52	3.08	0.00
74	7.31	4.57	6.34	8.01
75	1.51	0.00	0.00	0.00
77/144	0.88	0.35	0.50	6.00
81	1.09	0.00	0.00	6.40
82/151	1.91	1.08	1.47	8.71
83/119	0.00	0.00	0.00	0.00
85/154	0.69	0.34	0.38	4.28
87	2.55	1.40	1.79	12.99
92	0.00	0.00	0.00	0.00
95	4.60	2.84	3.68	5.83
97	1.68	0.72	1.00	5.90
99	4.09	2.11	2.57	10.74
100	1.78	1.68	2.20	1.52
105/141	1.37	0.76	0.95	6.12
108/123	0.26	0.00	0.00	0.00
110	5.25	3.40	4.19	20.91
114	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	5.03	4.21	3.27	20.38
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	0.47	0.00	0.00	10.90
128/185	0.00	0.00	0.00	0.00
129/178	0.00	0.00	0.00	0.00
130	0.00	0.14	0.00	0.00
131	0.99	0.46	0.00	12.52
134	0.00	0.00	0.00	0.00
135	1.97	1.12	1.15	7.33
136	0.00	0.00	0.00	0.00
137	0.00	0.16	0.00	0.00
138	8.26	4.39	3.06	27.60
146	2.19	1.07	1.32	32.22
147	0.00	0.00	0.00	0.00
149	5.31	2.96	3.99	23.53
132/153	4.19	2.41	2.79	17.93
156	0.00	0.00	0.00	0.00
157	0.00	0.00	0.00	0.00
158	1.29	0.28	0.31	0.00
159	532.48	464.68	612.00	6527.42
163	0.00	0.00	0.00	0.00
164	0.00	0.23	0.00	0.00
166	61.27	53.02	60.05	696.73
167	0.00	0.00	0.00	0.00
170	2.24	0.77	0.76	0.00

Sample ID Congener	NRPK A	NRPK B	NRPK C	NRPK 584
172	0.00	0.00	0.00	0.00
173	0.00	0.00	0.00	0.00
174	6.71	5.09	6.43	0.00
175	0.00	0.08	0.00	0.00
176	0.00	0.00	0.00	0.00
177	8.60	2.67	3.36	23.45
179	3.18	1.26	2.32	17.53
180	6.75	3.61	3.84	16.94
183/187	4.89	2.48	3.13	18.47
189	1.50	0.48	0.49	2.45
190	0.00	0.00	0.00	0.00
191	39.04	23.26	28.33	190.01
193	0.00	0.00	0.00	0.00
194	2.40	0.57	8.09	4.40
195/207	2.61	0.00	0.27	2.20
196/203	2.57	0.53	0.76	3.55
197	5.82	2.29	2.84	24.77
199	3.12	1.16	1.37	5.64
200	2.57	0.00	0.00	0.00
202	3.29	2.95	3.76	24.91
204	0.00	0.00	0.00	0.00
205	0.00	0.98	0.96	0.00
206	18.36	10.90	14.74	82.48
208	1.98	0.00	0.37	0.00
209	0.00	0.00	0.35	72.32

Sample ID	NRPK 598	NRPK 612	NRPK 614	660 NRPK
Total CB ($\text{ng/g}_{\text{lipid}}$)	881.34	920.78	1645.85	1341.79
%mono	0.00%	0.00%	0.00%	0.00%
%di	2.15%	4.88%	4.79%	50.62%
%tri	6.24%	20.40%	10.67%	20.09%
%tetra	13.60%	25.76%	17.44%	16.71%
%penta	12.19%	9.61%	9.37%	7.91%
%hexa	13.25%	5.71%	9.12%	2.42%
%hepta	20.19%	23.22%	28.26%	2.20%
%octa	19.75%	4.14%	12.47%	0.01%
%nona	12.63%	6.29%	7.61%	0.05%
%deca	0.00%	0.00%	0.28%	0.00%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	208.16
6	5.97	4.53	38.99	119.98
7	0.00	5.33	0.00	61.44
8	12.97	27.95	26.45	0.00
9	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00
13/27	0.00	3.40	0.00	4.11
14	0.00	5.46	13.39	287.61
15	0.00	0.00	0.00	0.00
16	6.63	21.43	17.83	0.00
17	12.81	36.18	29.94	38.04
18	0.00	0.00	0.00	0.00
19	0.00	11.87	23.14	137.44
20/33	0.00	0.00	0.00	0.00
22	5.14	31.24	22.61	21.23
24	0.00	7.59	13.39	20.17
25	3.17	8.84	8.46	0.00
26	3.12	12.55	12.08	0.00
28	0.00	0.00	0.00	0.00
29	8.04	17.79	13.09	0.00
30	325.57	246.42	261.35	0.00
31/53	6.88	36.90	25.70	46.34
32	10.38	12.45	14.33	27.47
34/54	0.00	4.75	9.71	0.00
35	0.00	2.68	0.00	0.00
37/40/103	6.89	8.11	9.25	0.00
41	0.00	6.33	8.17	0.00
42/59	0.00	5.65	7.02	8.04
44	17.44	31.11	35.29	54.14
45	0.00	7.33	9.90	0.00
46	0.00	4.55	7.08	4.58
47/104	0.00	0.00	0.00	0.00
48	0.00	10.43	10.97	19.00
49	6.67	14.48	13.70	27.48
51	0.00	0.00	0.00	11.92

Sample ID	NRPK 598	NRPK 612	NRPK 614	660 NRPK
Congener				
52	0.00	0.00	0.00	0.00
53	0.00	54.52	32.77	0.00
56/84	4.12	6.35	8.47	6.01
60/90/101	5.82	7.68	10.74	8.65
63/93	0.00	0.00	0.00	0.00
64	5.75	9.78	0.00	0.00
67	43.76	4.09	8.80	0.00
68/91	6.31	14.31	19.38	18.06
69	0.00	1.51	22.45	40.31
70	11.88	27.51	23.99	0.00
71	0.00	8.16	11.99	0.00
73	7.49	0.00	0.00	0.00
74	9.23	14.60	14.25	15.93
75	4.72	0.00	3.06	0.00
77/144	0.00	1.47	3.63	0.44
81	0.00	0.00	37.51	4.57
82/151	3.20	4.11	5.59	2.22
83/119	0.00	0.00	4.24	0.00
85/154	0.00	1.60	4.24	3.45
87	8.28	5.58	10.46	2.41
92	0.00	0.00	0.00	0.00
95	0.00	8.83	12.01	0.00
97	7.23	2.88	10.45	0.00
99	10.67	6.01	16.16	6.72
100	4.81	6.12	7.22	0.00
105/141	3.98	3.33	6.17	1.77
108/123	0.00	0.00	0.00	0.00
110	14.56	15.88	13.27	5.78
114	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	36.13	17.55	40.06	69.65
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	10.77	2.94	8.22	0.00
128/185	0.00	0.00	0.00	0.00
129/178	0.00	0.00	0.00	0.00
130	0.00	0.00	5.53	0.00
131	8.99	8.09	12.25	9.12
134	0.00	0.00	0.00	0.00
135	4.29	2.77	6.00	1.51
136	0.00	0.00	0.00	0.00
137	0.00	0.00	0.00	0.00
138	22.97	15.41	29.27	7.14
146	19.92	0.00	23.74	0.00
147	0.00	0.00	0.00	0.00
149	9.90	11.54	21.71	4.21
132/153	12.38	9.52	19.62	6.50
156	0.00	0.00	0.00	0.00
157	0.00	0.00	0.00	0.00
158	34.70	0.00	15.75	0.00
159	6305.17	6195.79	5847.95	15243.90
163	0.00	0.00	0.00	0.00
164	0.00	0.00	6.34	0.00
166	752.15	630.33	713.97	297.79
167	0.00	0.00	0.00	0.00
170	46.37	3.85	15.54	0.00

Sample ID **Congener**	NRPK 598	NRPK 612	NRPK 614	660 NRPK
172	0.00	0.00	0.00	16.42
173	0.00	0.00	0.00	0.00
174	0.00	0.00	87.05	0.00
175	0.00	0.00	0.00	0.00
176	0.00	0.00	0.00	0.00
177	0.00	22.15	39.90	0.00
179	0.00	4.80	26.64	2.10
180	28.89	16.92	65.82	5.20
183/187	15.81	9.34	16.02	1.95
189	0.00	2.78	33.45	0.45
190	23.72	0.00	0.00	0.00
191	63.19	153.94	180.63	3.35
193	0.00	0.00	0.00	0.00
194	52.34	1.85	23.85	0.15
195/207	26.39	0.00	0.00	0.00
196/203	18.63	7.94	17.08	0.00
197	28.34	19.45	37.76	0.00
199	26.09	6.44	21.87	0.00
200	35.49	0.00	0.00	0.00
202	0.00	0.00	0.00	0.00
204	0.00	0.00	0.00	0.00
205	0.00	2.42	104.63	0.00
206	57.99	57.89	125.18	0.62
208	40.14	0.00	0.00	0.00
209	0.00	0.00	4.63	0.00

Sample ID	**675 NRPK**	**573 NRPK**	**580 NRPK**	**620 NRPK**
Total CB (ng/g$_{lipid}$)	576.79	291.67	426.64	789.17
%mono	0.00%	0.00%	0.00%	0.00%
%di	26.67%	6.88%	0.32%	2.56%
%tri	10.98%	18.68%	1.39%	2.41%
%tetra	22.95%	16.54%	9.80%	5.20%
%penta	28.30%	20.77%	33.93%	27.09%
%hexa	5.96%	15.57%	26.71%	23.68%
%hepta	4.17%	13.92%	16.43%	25.12%
%octa	0.35%	5.71%	7.14%	8.83%
%nona	0.61%	1.79%	3.20%	4.65%
%deca	0.00%	0.15%	1.07%	0.46%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	3.23	0.00	0.00
5	40.26	0.00	0.00	0.00
6	50.87	1.46	0.85	1.06
7	14.99	0.55	0.00	0.00
8	0.00	11.49	0.49	3.66
9	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	14.96
12	0.00	0.00	0.00	0.00
13/27	0.00	6.69	0.00	1.05
14	47.72	0.00	0.00	0.00
15	0.00	0.00	0.00	0.00
16	10.21	1.02	0.00	0.00
17	0.00	8.38	0.31	1.41
18	0.00	0.00	0.00	0.00
19	12.66	9.81	0.58	1.39
20/33	0.00	0.00	0.00	0.00
22	8.58	3.00	1.18	0.81
24	3.25	0.73	0.00	0.00
25	4.67	3.69	0.70	0.00
26	0.00	7.54	0.64	3.34
28	0.00	0.00	0.00	0.00
29	0.00	1.17	0.73	4.64
30	0.00	35.27	26.99	41.70
31/53	15.18	8.10	1.12	3.53
32	11.58	10.49	0.27	3.73
34/54	4.97	1.53	0.42	1.21
35	0.00	0.00	0.00	0.00
37/40/103	6.90	1.46	2.25	2.41
41	5.41	0.59	0.00	1.22
42/59	4.84	1.40	1.29	0.34
44	27.37	3.96	4.95	2.62
45	0.00	2.22	0.00	0.00
46	0.00	1.39	0.00	0.00
47/104	0.00	0.00	0.00	0.00
48	7.94	0.95	0.00	0.00
49	13.27	6.00	1.73	2.59
51	0.00	2.51	0.00	0.00

Sample ID	**675 NRPK**	**573 NRPK**	**580 NRPK**	**620 NRPK**
Congener				
52	0.00	0.00	0.00	0.00
53	0.00	5.40	1.71	2.82
56/84	4.88	1.18	1.53	1.94
60/90/101	10.08	2.80	6.00	8.26
63/93	0.00	0.00	0.00	0.00
64	9.92	3.30	2.34	1.78
67	0.00	0.50	4.20	1.55
68/91	9.79	2.13	2.24	2.94
69	20.02	0.45	3.90	2.97
70	0.00	3.08	4.28	4.01
71	0.00	2.49	1.19	0.84
73	8.97	0.84	0.00	0.00
74	11.60	2.85	3.73	4.19
75	0.00	0.00	0.91	0.00
77/144	0.00	0.72	2.18	2.43
81	0.00	2.04	5.11	6.51
82/151	2.13	1.76	3.26	6.56
83/119	1.34	0.76	1.54	1.46
85/154	0.00	0.00	0.00	0.00
87	3.46	2.02	4.75	5.89
92	0.00	0.00	0.00	0.00
95	12.23	3.81	5.63	6.08
97	3.87	1.27	3.83	3.57
99	13.02	5.79	13.73	17.86
100	3.01	0.77	0.00	0.00
105/141	1.83	1.98	4.62	7.66
108/123	0.00	0.72	2.04	1.58
110	9.46	7.94	13.84	19.18
114	0.41	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	95.71	31.62	86.83	142.33
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	2.43	0.00	0.00	0.00
128/185	0.00	0.00	4.04	0.00
129/178	0.00	0.00	0.00	0.00
130	0.00	1.40	3.52	7.89
131	6.35	0.00	0.00	0.00
134	0.00	0.00	0.00	0.00
135	1.89	0.00	0.00	0.00
136	0.00	0.00	0.00	0.00
137	0.00	1.17	2.62	6.72
138	10.45	11.21	32.15	54.83
146	0.00	4.88	16.58	25.23
147	0.00	0.00	0.00	0.00
149	4.07	6.57	15.89	21.34
132/153	8.91	9.47	18.31	36.10
156	0.00	1.53	3.05	1.38
157	0.00	1.27	3.20	0.00
158	0.70	2.64	5.31	8.92
159	11820.33	480.91	520.24	2252.25
163	0.00	0.00	0.00	0.00
164	0.00	1.05	2.96	5.78
166	225.20	52.78	62.84	222.51
167	0.00	1.99	3.33	10.36
170	0.00	5.18	7.00	25.11

Sample ID	675 NRPK	573 NRPK	580 NRPK	620 NRPK
Congener				
172	13.08	0.00	0.00	0.00
173	0.00	0.00	4.08	0.00
174	0.00	3.19	4.33	16.44
175	0.00	1.42	3.75	8.06
176	0.00	0.00	0.00	0.00
177	0.00	4.07	6.45	28.58
179	0.55	2.47	4.81	15.15
180	5.56	10.81	22.60	44.36
183/187	2.66	5.31	12.27	31.37
189	0.58	1.36	0.00	10.60
190	0.00	2.80	4.82	9.77
191	1.64	3.98	0.00	8.80
193	0.00	0.00	0.00	0.00
194	0.22	2.90	5.63	2.53
195/207	1.21	1.70	3.08	17.92
196/203	0.39	2.50	5.80	10.30
197	0.00	2.83	3.68	0.00
199	0.81	3.95	6.43	15.99
200	0.00	0.00	0.00	0.00
202	0.00	2.68	4.70	16.07
204	0.00	0.00	0.00	0.00
205	0.00	0.96	2.70	15.86
206	2.91	2.57	7.27	7.91
208	0.00	1.80	4.84	19.86
209	0.00	0.45	4.56	3.60

Sample ID	NRPK 491	NRPK 742	NRPK 620	NRPK 815
Total CB (ng/g$_{lipid}$)	1172.78	1465.92	1187.68	278.28
%mono	0.00%	0.00%	0.00%	0.00%
%di	8.42%	8.21%	3.71%	5.82%
%tri	20.39%	21.26%	6.21%	19.39%
%tetra	23.89%	31.81%	11.31%	17.14%
%penta	10.98%	11.93%	40.18%	16.48%
%hexa	5.33%	9.86%	19.69%	11.81%
%hepta	20.72%	8.73%	14.40%	16.93%
%octa	5.31%	4.66%	2.73%	4.29%
%nona	4.96%	2.63%	0.82%	5.89%
%deca	0.00%	0.91%	0.97%	2.27%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00
6	10.38	14.12	21.43	7.19
7	30.45	17.44	0.00	0.00
8	28.58	20.56	20.36	4.72
9	0.00	0.00	0.00	0.00
10	6.32	1.91	2.25	0.00
12	0.00	0.00	0.00	0.00
13/27	7.89	0.00	0.00	0.00
14	19.10	66.34	0.00	4.27
15	0.00	0.00	0.00	0.00
16	25.52	38.10	0.00	6.28
17	45.30	54.43	2.44	2.48
18	0.00	0.00	0.00	0.00
19	32.07	47.37	0.00	0.00
20/33	0.00	0.00	0.00	0.00
22	15.17	23.54	4.22	2.60
24	14.49	16.71	0.00	0.00
25	8.66	20.29	0.00	0.00
26	9.78	18.49	4.16	0.00
28	0.00	0.00	0.00	0.00
29	30.84	38.04	17.56	11.93
30	383.40	281.94	256.36	244.09
31/53	20.60	38.05	7.75	4.13
32	16.58	20.24	33.45	24.48
34/54	5.20	17.04	13.48	7.19
35	19.57	0.00	0.00	0.00
37/40/103	12.95	20.75	4.04	1.61
41	12.70	24.57	1.72	0.88
42/59	7.47	12.50	2.74	0.94
44	39.56	58.25	15.95	6.50
45	10.73	29.49	1.44	1.41
46	14.31	0.00	0.00	0.00
47/104	0.00	0.00	0.00	0.00
48	14.70	22.27	3.91	1.65
49	15.05	21.05	7.31	3.01
51	2.69	0.00	0.00	0.00

Sample ID	**NRPK 491**	**NRPK 742**	**NRPK 620**	**NRPK 815**
Congener				
52	0.00	0.00	0.00	0.00
53	0.00	32.36	0.00	0.00
56/84	7.65	13.68	6.34	1.32
60/90/101	8.59	14.25	12.85	2.40
63/93	0.00	0.00	0.00	0.00
64	19.93	30.00	4.93	2.04
67	28.33	0.00	12.74	0.00
68/91	11.49	19.77	20.90	8.00
69	20.67	31.17	11.33	0.00
70	24.35	31.46	22.35	9.29
71	14.90	26.34	4.42	1.48
73	0.00	0.00	0.00	0.00
74	15.39	23.19	14.69	4.43
75	9.28	15.55	0.00	0.00
77/144	0.90	6.28	1.76	0.39
81	0.00	49.01	0.00	4.22
82/151	4.39	8.67	6.97	1.85
83/119	0.00	0.00	1.05	0.00
85/154	2.91	6.20	0.00	0.00
87	12.88	19.80	7.39	1.76
92	0.00	0.00	0.00	0.00
95	16.64	20.79	13.31	0.00
97	7.20	22.32	3.91	0.00
99	11.09	27.45	24.98	2.70
100	7.49	0.00	0.00	0.00
105/141	2.20	4.90	9.78	1.18
108/123	0.00	0.00	1.35	0.00
110	14.85	0.00	37.75	4.20
114	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	27.97	26.85	352.56	26.68
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	6.27	14.66	2.94	2.20
128/185	0.00	0.00	0.00	0.00
129/178	0.00	0.00	0.00	0.00
130	0.00	0.00	4.38	0.00
131	8.32	7.42	16.12	5.77
134	0.00	0.00	0.00	0.00
135	0.00	9.91	4.97	1.10
136	0.00	0.00	0.00	0.00
137	5.42	0.00	2.45	0.00
138	0.00	12.59	82.26	5.59
146	10.40	39.10	28.95	7.66
147	0.00	0.00	0.00	0.00
149	21.52	40.33	18.78	4.74
132/153	11.71	14.26	49.56	6.30
156	0.00	0.00	0.00	0.00
157	0.00	0.00	8.60	0.00
158	0.00	7.90	6.36	0.00
159	7473.84	7183.91	8601.41	5040.32
163	0.00	0.00	0.00	0.00
164	0.00	0.00	2.21	0.00
166	726.31	757.71	1100.41	468.86
167	0.00	0.00	0.00	0.00
170	0.00	5.69	13.31	1.29

Sample ID	NRPK 491	NRPK 742	NRPK 620	NRPK 815
Congener				
172	0.00	0.00	0.00	0.00
173	0.00	0.00	0.00	0.00
174	88.69	0.00	0.00	0.00
175	0.00	0.00	1.47	0.00
176	0.00	0.00	0.00	0.00
177	0.00	0.00	33.72	16.10
179	8.49	27.47	6.06	1.61
180	28.34	19.18	68.07	14.58
183/187	12.57	14.34	29.89	5.42
189	6.25	7.70	5.36	2.48
190	0.00	0.00	4.50	0.00
191	98.69	53.64	8.60	5.62
193	0.00	0.00	0.00	0.00
194	3.15	26.11	10.21	4.34
195/207	3.72	0.00	2.26	1.77
196/203	11.03	3.04	5.54	0.95
197	25.50	26.74	0.00	0.00
199	18.30	5.87	12.62	1.97
200	0.00	0.00	0.00	0.00
202	0.00	0.00	0.00	0.00
204	0.00	0.00	0.00	0.00
205	2.42	6.50	2.90	3.78
206	56.29	38.56	6.87	15.49
208	0.00	0.00	1.68	0.00
209	0.00	13.35	11.48	6.31

Sample ID	NRPK 638	NRPKL1	660 NRPK LIVER	675 NRPK LIVER
Total CB (ng/g$_{lipid}$)	1306.74	1010.24	1902.14	365.39
%mono	0.00%	0.00%	0.00%	0.00%
%di	38.01%	7.55%	3.33%	2.70%
%tri	12.37%	21.24%	6.27%	7.09%
%tetra	6.25%	24.34%	12.86%	11.70%
%penta	4.42%	15.61%	54.25%	54.39%
%hexa	10.85%	8.67%	13.34%	15.29%
%hepta	11.45%	14.92%	7.14%	5.97%
%octa	10.71%	4.96%	2.19%	2.11%
%nona	5.95%	2.64%	0.60%	0.69%
%deca	0.00%	0.07%	0.03%	0.05%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	4.35	0.00	0.00
5	0.00	0.00	0.00	0.00
6	82.30	7.41	63.25	9.87
7	0.00	8.82	0.00	0.00
8	140.42	52.42	0.00	0.00
9	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00
13/27	0.00	6.47	0.00	0.00
14	144.89	0.00	0.00	0.00
15	129.04	0.00	0.00	0.00
16	0.00	24.85	10.56	2.44
17	0.00	58.28	16.99	4.25
18	0.00	0.00	0.00	0.00
19	47.07	7.43	36.03	7.20
20/33	7.69	0.00	0.00	0.00
22	0.00	28.92	8.30	0.00
24	21.54	3.08	0.00	0.00
25	17.47	9.42	7.32	3.49
26	0.00	12.84	7.43	2.19
28	0.00	0.00	0.00	0.00
29	40.28	8.38	0.00	0.00
30	1132.20	64.98	0.00	0.00
31/53	20.18	27.57	15.13	3.77
32	13.47	40.28	13.87	2.03
34/54	0.00	3.53	9.98	2.35
35	0.00	0.00	0.00	0.00
37/40/103	12.11	6.89	18.67	3.73
41	0.00	8.30	0.00	0.00
42/59	0.00	6.58	3.57	0.75
44	0.00	27.83	30.97	3.86
45	0.00	9.60	0.00	0.00
46	0.00	6.69	0.00	0.00
47/104	0.00	0.00	0.00	0.00
48	0.00	12.71	0.00	0.00
49	0.00	16.17	24.30	4.01
51	12.60	0.00	0.00	1.24

Sample ID	NRPK 638	NRPKL1	660 NRPK LIVER	675 NRPK LIVER
Congener				
52	0.00	0.00	0.00	0.00
53	0.00	45.87	25.74	4.29
56/84	0.00	6.24	10.89	2.37
60/90/101	2.47	8.91	51.79	10.21
63/93	0.00	0.00	0.00	0.00
64	9.31	9.05	10.25	1.82
67	20.35	6.22	0.00	0.31
68/91	3.23	10.71	25.71	5.24
69	0.00	2.96	33.51	6.34
70	10.36	21.61	0.00	0.00
71	0.00	9.11	0.00	0.00
73	0.00	11.76	12.68	0.00
74	0.00	13.65	42.54	6.86
75	0.00	3.24	0.00	0.00
77/144	0.00	2.41	3.73	0.97
81	12.53	4.10	4.91	1.30
82/151	3.81	5.11	11.06	2.39
83/119	0.00	1.33	3.37	0.82
85/154	3.13	0.00	0.00	0.00
87	0.00	6.05	8.70	1.87
92	0.00	0.00	0.00	0.00
95	0.00	10.08	51.78	9.67
97	0.00	3.94	8.98	2.24
99	0.00	13.17	63.37	12.97
100	10.46	5.30	0.00	0.60
105/141	5.89	4.34	16.81	3.22
108/123	0.00	1.67	4.29	1.21
110	0.00	17.43	45.24	9.53
114	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	21.15	77.27	770.37	143.06
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	12.38	0.00	2.83	0.00
128/185	0.00	0.00	0.00	4.18
129/178	0.00	0.00	0.00	0.00
130	0.00	0.00	6.11	1.32
131	12.59	0.00	0.00	4.40
134	0.00	0.00	0.00	0.00
135	0.00	5.52	13.69	3.05
136	0.00	0.00	0.00	0.00
137	15.66	3.10	6.44	1.31
138	20.24	17.17	80.10	15.41
146	24.53	9.53	0.00	0.00
147	0.00	0.00	0.00	0.00
149	25.35	17.88	33.44	6.71
132/153	10.56	17.62	65.23	12.03
156	0.00	0.00	0.00	0.00
157	0.00	3.06	0.00	0.92
158	13.49	4.49	11.82	2.39
159	12106.54	799.11	11627.91	1279.10
163	0.00	0.00	0.00	0.00
164	12.94	3.29	4.35	0.89
166	1672.11	109.34	238.04	31.43
167	0.00	0.00	16.74	2.08
170	0.00	9.77	0.00	0.00

Sample ID **Congener**	NRPK 638	NRPKL1	660 NRPK LIVER	675 NRPK LIVER
172	0.00	0.00	25.08	3.74
173	0.00	0.00	0.00	0.00
174	0.00	12.28	20.39	3.01
175	0.00	3.38	5.29	1.13
176	0.00	0.00	0.00	0.00
177	0.00	8.26	13.85	2.03
179	7.87	10.32	4.69	0.82
180	47.64	21.89	27.48	4.83
183/187	21.02	17.16	21.92	4.22
189	0.00	3.54	2.30	0.44
190	0.00	5.14	6.54	1.09
191	73.10	59.00	8.21	0.51
193	0.00	0.00	0.00	0.00
194	25.31	6.26	1.06	0.18
195/207	0.00	4.01	11.38	2.15
196/203	0.00	10.66	9.70	1.68
197	51.54	6.68	0.00	0.00
199	0.00	10.01	9.81	1.87
200	0.00	5.47	0.00	0.00
202	0.00	7.73	13.52	1.91
204	0.00	0.00	0.00	0.00
205	63.07	1.27	1.82	1.00
206	77.72	20.49	4.56	1.27
208	0.00	4.21	1.12	0.18
209	0.00	0.72	0.61	0.20

Sample ID	NRPK742L	NRPK620L2	NRPK815L	NRPK638L
Total CB (ng/g$_{lipid}$)	403.93	416.02	320.60	262.33
%mono	0.00%	0.00%	0.00%	0.00%
%di	3.11%	1.08%	1.66%	7.67%
%tri	6.66%	2.69%	3.96%	6.65%
%tetra	14.70%	8.51%	7.86%	26.74%
%penta	36.35%	36.64%	34.59%	20.97%
%hexa	16.61%	24.94%	17.49%	15.42%
%hepta	14.05%	15.99%	20.54%	13.50%
%octa	5.79%	5.74%	7.36%	6.30%
%nona	2.64%	3.65%	5.65%	2.29%
%deca	0.10%	0.76%	0.89%	0.45%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00
6	0.94	2.33	0.42	8.99
7	3.66	0.00	0.56	0.00
8	4.71	2.15	1.95	5.64
9	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	2.45	0.00	0.00	0.00
13/27	1.59	0.00	0.71	0.00
14	0.00	0.00	2.04	0.00
15	0.00	0.00	0.00	5.50
16	2.61	1.19	1.39	0.00
17	3.82	1.97	2.15	2.37
18	0.00	0.00	0.00	0.00
19	3.06	0.00	0.00	1.29
20/33	0.00	1.36	1.47	1.83
22	4.17	1.36	1.34	1.90
24	0.00	0.00	0.57	0.00
25	2.38	0.00	1.21	0.58
26	2.55	1.65	1.07	0.00
28	0.00	0.00	0.00	0.00
29	1.81	0.53	0.00	5.13
30	43.22	37.08	56.08	196.85
31/53	3.78	1.92	2.04	0.00
32	2.59	1.07	1.60	3.09
34/54	1.24	0.99	0.00	1.44
35	0.00	0.00	0.00	0.00
37/40/103	1.87	1.90	1.57	1.60
41	2.05	1.39	1.00	0.00
42/59	1.59	0.77	0.65	1.78
44	5.96	4.29	3.66	5.40
45	2.38	1.30	1.22	0.00
46	1.64	0.00	0.00	0.00
47/104	0.00	0.00	0.00	0.00
48	2.28	0.00	0.00	0.00
49	3.74	2.47	2.74	11.89
51	0.00	0.00	0.00	0.00

Sample ID **Congener**	**NRPK742L**	**NRPK620L2**	**NRPK815L**	**NRPK638L**
52	0.00	0.00	0.00	0.00
53	5.11	0.00	0.00	2.43
56/84	1.72	1.27	1.36	0.78
60/90/101	5.55	5.18	4.64	1.90
63/93	0.00	0.00	0.00	0.00
64	3.01	2.17	1.41	2.48
67	2.88	0.00	0.00	1.82
68/91	2.33	2.47	1.99	1.33
69	4.80	2.98	0.00	10.44
70	4.65	3.12	3.05	2.61
71	1.66	1.03	0.98	0.00
73	2.45	1.75	0.00	25.48
74	3.55	3.28	2.23	2.38
75	0.00	0.00	0.00	0.00
77/144	1.59	1.35	0.99	1.02
81	3.82	4.49	3.01	0.00
82/151	2.70	2.72	2.57	1.59
83/119	0.91	0.95	0.42	0.00
85/154	0.00	0.00	0.00	0.00
87	3.52	3.34	2.63	2.20
92	0.00	0.00	0.00	0.00
95	4.63	4.31	3.85	2.59
97	2.54	2.93	1.28	1.80
99	10.28	11.93	7.32	5.87
100	1.69	0.00	0.00	0.00
105/141	3.29	3.97	2.91	1.42
108/123	1.37	1.47	0.63	0.55
110	12.35	12.78	9.73	6.04
114	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	98.69	103.31	76.36	30.11
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	0.00	0.00	0.64	1.49
128/185	2.99	4.25	0.00	0.00
129/178	2.73	0.00	0.00	0.00
130	2.19	2.78	1.37	0.00
131	0.00	0.00	0.00	2.35
134	0.00	0.00	0.00	0.00
135	0.00	3.87	2.94	2.75
136	0.00	0.00	0.00	0.00
137	2.17	2.13	1.29	0.00
138	13.77	30.56	11.08	12.36
146	11.93	14.00	8.10	7.62
147	0.00	0.00	0.00	0.00
149	6.74	11.60	6.20	7.01
132/153	15.27	17.99	12.61	6.36
156	1.27	2.53	0.00	0.00
157	2.10	2.18	1.97	0.00
158	0.00	4.76	2.72	0.00
159	383.20	550.06	694.83	1621.27
163	0.00	0.00	0.00	0.00
164	2.25	2.04	1.47	0.00
166	68.20	83.56	99.96	237.15
167	2.76	3.17	3.09	0.00
170	5.67	6.46	4.98	2.52

Sample ID	NRPK742L	NRPK620L2	NRPK815L	NRPK638L
Congener				
172	0.00	0.00	0.00	0.00
173	3.95	0.00	4.20	0.00
174	3.36	4.65	5.02	0.00
175	2.94	2.80	2.38	1.17
176	0.00	0.00	0.00	0.00
177	4.76	5.60	5.38	5.79
179	4.16	4.85	4.08	4.43
180	17.71	20.50	17.15	8.21
183/187	10.11	11.53	9.80	4.61
189	1.34	1.73	1.43	1.29
190	0.00	3.82	3.41	0.00
191	1.40	4.62	8.02	7.41
193	0.00	0.00	0.00	0.00
194	1.78	4.09	3.77	1.51
195/207	2.22	2.44	2.14	0.92
196/203	4.50	4.74	4.31	2.03
197	2.85	0.00	3.28	7.09
199	9.45	5.75	5.05	4.60
200	0.00	0.00	0.00	0.00
202	3.61	4.30	4.75	0.00
204	0.00	0.00	0.00	0.00
205	0.09	3.76	1.38	0.85
206	6.37	10.59	14.07	4.71
208	3.18	3.39	2.96	0.85
209	0.39	3.14	2.85	1.18

Sample ID	CHICK	CHICK637	CHICK1472	CHICKLIV
Total CB (ng/g$_{lipid}$)	2546.19	2618.20	2166.24	2477.34
%mono	0.00%	0.00%	0.00%	0.00%
%di	11.05%	4.66%	3.70%	2.15%
%tri	11.12%	2.36%	5.58%	0.77%
%tetra	11.33%	4.95%	9.43%	3.33%
%penta	34.38%	63.57%	43.65%	37.86%
%hexa	13.35%	13.65%	13.99%	15.47%
%hepta	10.40%	7.51%	18.13%	19.73%
%octa	5.66%	2.57%	4.58%	11.30%
%nona	1.28%	0.55%	0.70%	6.45%
%deca	1.42%	0.16%	0.25%	2.94%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00
6	5.99	57.25	57.66	16.76
7	86.44	0.00	0.00	0.00
8	17.84	39.16	2.99	36.56
9	0.00	0.00	0.00	0.00
10	0.00	14.42	0.00	0.00
12	0.00	0.00	0.00	0.00
13/27	0.00	0.29	0.00	0.00
14	171.20	11.00	19.47	0.00
15	0.00	0.00	0.00	0.00
16	29.31	3.10	10.33	1.58
17	27.43	3.46	3.03	0.00
18	0.00	10.90	9.49	0.00
19	49.50	0.00	0.00	0.00
20/33	0.00	5.22	4.14	0.00
22	15.24	3.28	2.97	1.87
24	10.50	0.00	0.00	0.00
25	41.78	0.00	0.00	0.00
26	22.16	0.00	0.00	0.00
28	0.00	19.07	15.64	0.00
29	37.70	11.27	43.50	6.90
30	471.18	0.00	0.00	53.25
31/53	20.02	0.00	0.00	2.63
32	19.56	2.79	15.76	3.44
34/54	27.17	4.48	25.64	5.02
35	0.00	0.00	0.00	0.00
37/40/103	19.07	1.32	9.44	4.66
41	0.00	0.95	0.00	0.99
42/59	15.95	1.36	1.39	0.40
44	28.80	9.03	9.47	3.99
45	15.66	2.79	1.96	0.00
46	0.00	0.00	0.00	0.00
47/104	0.00	4.04	2.64	0.00
48	0.00	5.25	2.62	0.00
49	12.07	6.95	4.35	8.28
51	39.96	0.00	0.00	1.18

Sample ID	CHICK	CHICK637	CHICK1472	CHICKLIV
Congener				
52	0.00	19.02	10.17	0.00
53	0.00	8.73	7.81	0.00
56/84	15.44	0.87	1.22	1.43
60/90/101	6.98	2.42	3.23	3.46
63/93	0.00	0.41	0.97	0.00
64	0.00	2.92	2.95	1.48
67	43.56	0.00	0.20	0.00
68/91	13.78	8.68	227.89	8.92
69	21.59	35.89	2.15	2.10
70	22.74	4.85	0.00	3.59
71	0.00	2.05	2.16	0.00
73	0.00	0.00	0.00	0.00
74	28.03	18.80	21.74	14.07
75	0.00	0.00	0.00	0.00
77/144	0.00	1.27	0.00	0.00
81	13.28	0.00	4.01	34.74
82/151	14.94	0.00	0.00	4.64
83/119	0.00	0.00	0.00	0.00
85/154	0.00	0.00	0.00	0.00
87	0.00	0.00	3.80	0.00
92	0.00	0.00	0.00	0.00
95	0.00	0.00	0.00	0.00
97	15.95	0.00	0.83	0.00
99	50.11	38.31	29.14	38.43
100	3.07	0.00	0.00	0.00
105/141	12.45	12.53	10.75	16.11
108/123	3.39	3.15	3.37	4.28
110	37.19	0.00	8.88	0.00
114	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	726.30	1595.56	759.11	865.73
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	0.00	0.00	1.30	0.00
128/185	0.00	24.11	24.01	19.95
129/178	0.00	0.00	34.03	0.00
130	0.00	1.44	35.15	26.83
131	0.00	45.96	36.72	0.00
134	0.00	0.00	0.00	0.00
135	0.00	0.00	0.00	0.00
136	0.00	0.00	0.00	0.00
137	0.00	3.06	2.28	12.82
138	101.21	124.72	0.00	89.48
146	38.64	41.62	65.43	69.31
147	0.00	0.00	10.27	0.00
149	30.97	1.61	0.00	10.61
153	95.69	85.91	88.10	91.28
156	15.47	0.00	0.00	14.75
157	0.00	12.54	9.96	0.00
158	8.48	8.04	8.73	22.27
159	5186.72	3107.52	3270.11	2606.88
163	0.00	0.00	0.00	0.00
164	0.00	0.00	0.72	3.80
166	778.95	616.72	653.61	441.32
167	35.87	13.63	11.24	21.71
170	47.06	35.14	46.53	70.71

Sample ID Congener	CHICK	CHICK637	CHICK1472	CHICKLIV
172	0.00	0.00	0.00	0.00
173	0.00	6.47	0.00	0.00
174	0.00	0.00	0.00	20.42
175	0.00	0.00	4.02	15.93
176	0.00	0.00	0.00	0.00
177	26.77	10.38	51.97	59.39
179	0.00	0.00	2.83	24.40
180	125.47	97.78	130.03	120.57
183/187	33.24	29.50	124.22	100.79
189	8.47	1.91	2.31	34.63
190	23.91	13.62	11.93	20.55
191	0.00	1.86	1.81	21.30
193	0.00	0.00	0.00	0.00
194	28.22	27.82	33.15	39.26
195/207	7.67	3.92	4.98	29.10
196/203	19.78	9.71	11.91	21.66
197	0.00	0.00	5.62	16.10
199	34.02	22.83	38.44	36.97
200	0.00	0.00	0.00	0.00
202	0.00	0.00	7.54	19.38
204	0.00	0.00	0.00	0.00
205	58.20	5.09	0.00	132.11
206	28.74	9.48	8.68	105.59
208	0.00	3.03	4.04	39.70
209	36.16	4.20	5.46	72.76

Sample ID	DCCO1111	DCCO637L	1472 LIVER	DCCO060718
Total CB (ng/g_{lipid})	2926.52	890.26	2166.24	1533.44
%mono	0.00%	0.00%	0.00%	0.00%
%di	0.24%	4.39%	3.70%	0.65%
%tri	0.39%	6.30%	5.58%	0.70%
%tetra	0.76%	11.47%	9.43%	5.85%
%penta	64.12%	33.77%	43.65%	39.23%
%hexa	11.73%	20.79%	13.99%	17.26%
%hepta	16.84%	17.73%	18.13%	25.09%
%octa	5.05%	4.38%	4.58%	7.77%
%nona	0.82%	1.07%	0.70%	2.88%
%deca	0.06%	0.11%	0.25%	0.58%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00
6	4.26	11.73	57.66	0.38
7	0.00	0.00	0.00	0.00
8	1.56	22.45	2.99	2.50
9	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00
13/27	0.00	0.00	0.00	0.00
14	1.33	4.88	19.47	0.00
15	0.00	0.00	0.00	7.07
16	1.06	6.40	10.33	1.17
17	0.83	3.00	3.03	2.83
18	0.00	0.00	9.49	0.00
19	2.41	8.57	0.00	0.00
20/33	0.00	1.26	4.14	1.63
22	0.49	0.00	2.97	0.00
24	0.00	0.00	0.00	0.78
25	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00
28	0.00	0.00	15.64	0.00
29	2.13	11.48	43.50	1.53
30	85.20	101.41	0.00	129.34
31/53	0.63	0.00	0.00	1.67
32	3.32	21.62	15.76	1.20
34/54	1.04	5.29	25.64	0.71
35	0.00	0.00	0.00	0.00
37/40/103	1.30	3.24	9.44	1.30
41	0.00	0.00	0.00	0.00
42/59	0.00	2.65	1.39	0.00
44	0.69	8.23	9.47	31.26
45	0.00	0.00	1.96	0.00
46	0.00	0.00	0.00	0.00
47/104	0.00	0.00	2.64	0.00
48	0.00	0.00	2.62	0.00
49	2.12	2.96	4.35	6.49
51	0.37	1.92	0.00	0.00

Sample ID	DCCO1111	DCCO637L	1472 LIVER	DCCO060718
Congener				
52	0.00	0.00	10.17	0.00
53	0.00	2.83	7.81	0.00
56/84	0.00	0.00	1.22	0.00
60/90/101	0.94	0.00	3.23	0.00
63/93	0.00	0.00	0.97	0.00
64	0.42	0.00	2.95	0.52
67	0.00	0.00	0.20	0.00
68/91	3.03	8.58	227.89	2.92
69	1.29	11.17	2.15	0.00
70	1.31	6.25	0.00	1.90
71	0.00	0.00	2.16	5.83
73	3.69	28.36	0.00	1.93
74	7.10	12.70	21.74	11.65
75	0.00	4.59	0.00	25.65
77/144	4.04	0.00	0.00	2.70
81	0.00	12.44	4.01	0.00
82/151	0.00	0.00	0.00	4.10
83/119	0.83	0.00	0.00	0.00
85/154	0.00	0.00	0.00	0.00
87	0.00	0.00	3.80	0.00
92	0.00	0.00	0.00	0.00
95	0.00	0.00	0.00	0.00
97	0.29	0.00	0.83	0.00
99	25.79	20.95	29.14	22.17
100	0.00	0.00	0.00	0.00
105/141	10.81	7.76	10.75	10.59
108/123	2.60	1.47	3.37	2.25
110	0.00	0.00	8.88	0.00
114	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	1834.49	267.87	759.11	562.74
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	0.00	1.07	1.30	0.00
128/185	8.75	0.00	24.01	10.25
129/178	0.00	0.00	34.03	0.00
130	12.35	7.17	35.15	0.00
131	11.13	11.09	36.72	15.79
134	0.00	0.00	0.00	0.00
135	12.91	0.00	0.00	0.00
136	0.00	0.00	0.00	0.00
137	4.41	2.36	2.28	0.00
138	87.13	49.28	0.00	87.89
146	59.52	24.36	65.43	31.56
147	6.32	2.42	10.27	0.00
149	4.60	0.64	0.00	7.07
153	95.48	43.92	88.10	88.11
156	0.00	0.00	0.00	0.00
157	7.12	10.05	9.96	9.65
158	20.88	7.99	8.73	0.00
159	500.00	3107.52	3270.11	1130.97
163	0.00	0.00	0.00	0.00
164	1.92	0.00	0.72	0.00
166	139.77	275.93	653.61	220.43
167	7.64	21.92	11.24	10.83
170	61.03	20.22	46.53	41.14

Sample ID	**DCCO1111**	**DCCO637L**	**1472 LIVER**	**DCCO060718**
Congener				
172	0.00	0.00	0.00	0.00
173	0.00	0.00	0.00	7.35
174	0.00	0.00	0.00	9.04
175	8.21	2.27	4.02	0.00
176	0.00	0.00	0.00	0.00
177	27.72	18.66	51.97	93.01
179	0.00	5.20	2.83	14.81
180	220.88	60.65	130.03	143.41
183/187	129.95	32.12	124.22	39.72
189	3.40	2.83	2.31	4.96
190	30.02	7.36	11.93	22.34
191	11.59	8.55	1.81	8.95
193	0.00	0.00	0.00	0.00
194	38.36	9.44	33.15	33.02
195/207	10.47	2.23	4.98	12.29
196/203	35.68	6.86	11.91	25.67
197	5.51	8.90	5.62	12.41
199	54.19	12.05	38.44	36.47
200	0.00	0.00	0.00	0.00
202	3.82	0.00	7.54	0.00
204	0.00	0.00	0.00	0.00
205	4.94	0.59	0.00	5.38
206	12.32	7.20	8.68	26.15
208	6.37	1.21	4.04	11.92
209	1.74	1.00	5.46	8.82

Sample ID	DCCO060727	dccoa	dccob	dccoaliv
Total CB (ng/g_{lipid})	5631.45	2794.79	6185.59	3892.70
%mono	0.00%	0.00%	0.00%	0.00%
%di	0.11%	4.74%	0.41%	3.67%
%tri	0.16%	0.52%	0.47%	1.04%
%tetra	2.30%	1.71%	1.01%	1.94%
%penta	38.96%	50.25%	4.06%	33.94%
%hexa	22.86%	16.92%	25.44%	19.83%
%hepta	25.18%	17.47%	47.76%	28.40%
%octa	8.49%	6.46%	16.39%	7.60%
%nona	1.72%	1.56%	3.43%	2.68%
%deca	0.22%	0.36%	1.04%	0.89%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00
6	3.58	13.61	25.15	19.49
7	0.00	0.00	0.00	0.00
8	2.82	118.77	125.67	123.32
9	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00
13/27	0.00	0.00	0.00	0.00
14	0.00	0.00	0.00	0.00
15	0.00	0.00	0.00	0.00
16	1.03	0.00	0.00	0.00
17	1.59	0.00	0.00	0.00
18	0.00	0.00	5.83	6.20
19	0.00	0.00	0.00	0.00
20/33	0.00	0.00	0.00	2.08
22	1.08	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00
28	0.00	13.89	17.13	15.84
29	2.10	0.00	4.52	8.17
30	122.65	0.00	0.00	0.00
31/53	1.11	0.00	0.00	0.00
32	1.25	0.00	0.00	0.00
34/54	1.25	0.49	1.75	11.71
35	0.00	0.00	0.00	0.00
37/40/103	1.58	1.56	3.07	7.36
41	0.00	0.00	0.00	0.00
42/59	0.00	0.00	0.00	0.00
44	0.00	1.13	0.96	7.20
45	0.00	0.00	0.00	0.00
46	0.37	0.00	0.00	0.00
47/104	0.00	2.33	3.63	2.91
48	0.00	0.00	0.00	0.00
49	9.77	0.00	0.72	1.97
51	0.00	0.00	0.00	0.00

Sample ID	DCCO060727	dccoa	dccob	dccoaliv
Congener				
52	0.00	0.00	1.35	4.30
53	0.00	0.95	1.17	2.94
56/84	0.71	0.00	0.00	1.27
60/90/101	1.80	1.13	2.76	2.89
63/93	0.00	0.44	0.00	0.00
64	0.00	0.41	0.00	0.00
67	0.00	1.17	0.00	0.00
68/91	14.09	13.71	17.11	17.60
69	3.55	0.00	0.00	0.00
70	0.00	0.00	2.94	6.30
71	0.00	0.00	0.00	0.00
73	0.00	0.00	0.00	0.00
74	38.45	34.31	40.03	31.78
75	62.95	0.00	0.70	0.00
77/144	9.93	1.04	2.36	1.92
81	0.00	0.00	0.00	0.00
82/151	0.00	0.00	0.00	0.00
83/119	3.41	0.00	0.00	0.00
85/154	0.00	0.00	0.00	0.00
87	0.00	0.00	0.00	0.00
92	0.00	0.00	0.00	0.00
95	0.00	2.40	0.58	0.00
97	0.00	0.00	0.00	0.00
99	118.06	93.39	143.90	92.84
100	0.00	0.00	0.00	0.00
105/141	58.62	34.30	78.65	46.98
108/123	8.03	7.36	12.55	13.65
110	0.00	0.00	0.00	0.00
114	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00
117	2012.58	1261.73	3006.17	1149.89
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	0.00	1.29	3.31	5.48
128/185	26.62	23.24	76.25	41.18
129/178	0.00	0.00	0.00	114.36
130	21.79	7.00	22.24	108.28
131	0.00	80.01	137.89	81.23
134	0.00	0.00	0.00	0.00
135	0.00	0.00	0.00	0.00
136	0.00	0.00	0.00	0.00
137	20.72	8.99	28.24	12.31
138	506.79	0.00	0.00	0.00
146	186.04	96.80	366.23	187.72
147	0.00	0.00	0.00	0.00
149	6.34	0.00	1.56	6.78
153	358.13	194.35	723.19	181.62
156	0.00	0.00	0.00	0.00
157	28.68	12.42	42.39	21.80
158	76.52	23.54	96.17	45.81
159	1130.97	830.29	1420.46	1137.92
163	0.00	0.00	0.00	0.00
164	7.67	1.69	7.24	0.00
166	292.06	188.95	488.46	279.16
167	27.10	18.95	69.88	24.30
170	185.43	88.16	496.49	101.74

Sample ID Congener	DCCO060727	dccoa	dccob	dccoaliv
172	0.00	0.00	0.00	0.00
173	11.72	0.00	18.41	8.29
174	0.00	0.00	0.00	0.00
175	24.98	5.51	29.30	24.98
176	0.00	0.00	0.00	0.00
177	75.51	22.38	103.71	190.36
179	0.00	0.00	0.00	0.00
180	657.76	247.30	1478.63	263.72
183/187	263.38	85.15	476.34	399.39
189	12.45	4.77	26.95	10.30
190	97.90	28.14	200.98	37.86
191	88.96	6.90	123.46	11.83
193	0.00	0.00	0.00	0.00
194	126.93	65.46	343.40	88.65
195/207	39.24	13.11	80.63	22.00
196/203	106.83	32.42	226.31	47.67
197	21.01	4.11	22.95	14.26
199	156.83	61.66	343.08	106.03
200	0.00	0.00	0.00	0.00
202	29.69	5.89	21.89	16.85
204	0.00	0.00	0.00	0.00
205	17.18	4.56	15.97	11.57
206	52.31	28.89	126.15	59.39
208	25.05	8.07	45.43	33.89
209	12.19	9.95	64.06	34.47

Sample ID	dccobliv	DCCOLIV060727	DCCOLIV060718	EGG 060519
Total CB (ng/g_{lipid})	4679.17	5078.22	941.19	5523.13
%mono	0.00%	0.00%	0.00%	0.00%
%di	0.50%	0.10%	4.09%	0.03%
%tri	0.76%	0.10%	8.11%	0.17%
%tetra	1.18%	0.75%	6.77%	4.35%
%penta	27.15%	30.75%	26.07%	10.22%
%hexa	18.08%	19.94%	10.64%	35.64%
%hepta	39.69%	34.48%	29.23%	33.31%
%octa	9.96%	10.36%	10.18%	12.67%
%nona	2.08%	3.10%	4.28%	3.27%
%deca	0.60%	0.42%	0.63%	0.35%
	100.00%	100.00%	100.00%	100.00%
Congener				
1	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00
6	18.01	4.43	2.36	0.00
7	0.00	0.00	3.50	0.00
8	1.29	0.00	9.91	1.51
9	0.00	0.00	0.00	0.00
10	0.00	0.40	0.00	0.00
12	0.02	0.00	0.00	0.00
13/27	0.16	0.00	0.00	0.00
14	4.10	0.00	0.00	0.00
15	0.00	0.00	22.74	0.00
16	1.45	0.00	11.40	0.00
17	1.91	0.08	7.34	0.00
18	6.15	0.00	0.00	0.00
19	0.00	0.00	0.00	0.00
20/33	1.95	0.00	2.18	0.00
22	1.65	0.00	2.14	0.00
24	0.09	0.00	0.00	0.00
25	0.00	0.00	1.08	0.00
26	0.00	0.00	1.29	0.00
28	10.74	0.00	0.00	0.00
29	5.87	0.00	10.99	6.76
30	0.00	6.73	311.84	8.18
31/53	0.00	0.00	0.00	0.00
32	1.37	3.59	33.19	0.74
34/54	5.74	1.09	10.12	2.42
35	0.00	0.00	0.00	0.00
37/40/103	4.35	2.20	5.12	2.34
41	0.00	0.00	0.00	1.18
42/59	0.61	0.29	1.57	0.10
44	4.53	1.37	8.74	1.51
45	1.11	0.00	0.00	0.00
46	0.00	0.00	0.00	0.00
47/104	1.96	0.00	0.00	0.00
48	0.00	0.00	0.00	0.00
49	0.75	0.79	2.50	0.00
51	1.53	0.37	1.08	0.00

Sample ID **Congener**	**dccobliv**	**DCCOLIV060727**	**DCCOLIV060718**	**EGG 060519**
52	5.05	0.00	0.00	0.00
53	3.86	0.00	3.74	14.31
56/84	0.57	0.66	1.07	1.48
60/90/101	1.93	2.13	1.25	4.49
63/93	0.41	0.00	0.00	0.00
64	1.64	0.00	0.00	0.00
67	0.00	0.00	0.00	0.30
68/91	7.93	10.44	8.96	12.47
69	0.00	0.00	2.96	0.00
70	2.93	0.00	11.88	0.00
71	0.96	0.00	0.00	0.00
73	0.00	0.00	0.00	0.00
74	17.54	25.02	15.44	18.54
75	0.00	0.00	3.41	2.46
77/144	0.88	5.73	0.51	19.47
81	3.80	0.00	0.00	181.76
82/151	0.00	0.00	2.69	23.44
83/119	0.00	3.46	0.00	7.69
85/154	0.00	0.00	0.00	791.19
87	0.00	0.00	1.65	0.00
92	0.00	0.00	0.00	0.00
95	0.00	0.00	0.00	0.00
97	0.28	2.11	0.00	0.00
99	60.65	91.92	9.27	80.59
100	0.00	0.00	0.00	0.98
105/141	34.48	55.30	5.49	57.41
108/123	6.47	8.70	1.18	15.67
110	8.56	0.00	6.65	0.00
114	0.00	0.00	8.84	0.00
115	0.00	0.00	0.00	0.00
117	1144.64	1402.34	206.12	0.00
118	0.00	0.00	0.00	0.00
122/165	0.00	0.00	0.00	0.00
124	1.90	0.00	0.00	0.00
128/185	44.67	35.36	0.00	25.58
129/178	121.56	0.00	18.20	0.00
130	60.23	83.96	12.47	38.22
131	61.84	0.00	8.89	0.00
134	0.00	0.00	0.00	0.00
135	0.00	0.00	1.63	0.00
136	0.00	0.00	0.00	0.00
137	11.03	19.64	3.10	29.38
138	0.00	257.21	0.00	596.31
146	211.28	211.94	0.00	189.68
147	0.00	10.70	0.00	30.72
149	2.87	8.62	10.28	30.32
153	291.07	303.93	37.76	396.77
156	0.00	0.00	0.00	17.62
157	23.36	37.05	5.68	37.66
158	51.51	0.00	0.00	106.53
159	1135.59	1734.31	2021.84	262.00
163	0.00	0.00	0.00	0.00
164	0.00	0.00	0.00	11.52
166	342.00	435.31	334.11	220.58
167	32.09	31.34	6.86	25.05
170	210.33	180.67	0.00	234.50

Sample ID **Congener**	**dccobliv**	**DCCOLIV060727**	**DCCOLIV060718**	**EGG 060519**
172	0.00	0.00	0.00	0.00
173	12.36	15.67	4.59	16.54
174	0.00	0.00	12.34	0.00
175	28.13	44.29	2.68	39.68
176	0.00	0.00	6.81	0.00
177	219.67	150.80	27.72	52.78
179	0.00	0.00	9.93	0.00
180	594.49	612.84	71.69	935.68
183/187	601.19	585.46	98.13	344.26
189	10.11	17.79	6.60	18.81
190	83.69	96.72	13.44	137.82
191	36.46	46.76	12.06	59.54
193	0.00	0.00	0.00	0.00
194	138.49	131.21	17.05	165.97
195/207	33.45	53.79	8.50	66.54
196/203	89.11	113.45	15.74	213.18
197	14.99	26.69	8.56	19.01
199	181.88	176.62	33.95	206.84
200	0.00	0.00	0.00	0.00
202	13.54	25.03	11.08	23.43
204	0.00	0.00	0.00	0.00
205	11.39	26.02	5.19	37.82
206	58.52	93.14	26.22	90.14
208	22.03	37.57	9.79	57.14
209	28.02	21.57	5.92	19.31

Sample ID	**EGG 060710**	**EGG 060727**
Total CB (ng/g$_{lipid}$)	4715.83	4255.31
%mono	0.00%	0.00%
%di	0.04%	0.03%
%tri	0.37%	0.22%
%tetra	13.96%	5.91%
%penta	14.86%	18.47%
%hexa	39.91%	42.60%
%hepta	19.89%	22.27%
%octa	8.04%	7.99%
%nona	2.66%	2.31%
%deca	0.25%	0.20%
	100.00%	100.00%
Congener		
1	0.00	0.00
4	0.00	0.00
5	0.00	0.00
6	0.00	0.03
7	0.00	0.00
8	2.06	1.08
9	0.00	0.00
10	0.00	0.00
12	0.00	0.00
13/27	0.00	0.00
14	0.00	0.00
15	0.00	0.00
16	0.37	0.21
17	0.00	0.27
18	0.00	0.00
19	0.00	0.00
20/33	0.00	0.00
22	0.00	0.60
24	0.39	0.00
25	0.35	0.20
26	0.24	0.12
28	0.00	0.00
29	2.75	6.42
30	14.82	12.03
31/53	0.33	0.00
32	0.68	0.64
34/54	0.78	0.76
35	11.40	0.00
37/40/103	2.15	1.56
41	0.99	1.21
42/59	0.15	0.15
44	1.30	0.91
45	1.62	0.00
46	0.72	1.09
47/104	0.00	0.00
48	0.00	0.00
49	0.51	0.38
51	1.43	0.58

Sample ID	EGG 060710	EGG 060727
Congener		
52	0.00	0.00
53	0.00	0.51
56/84	2.28	1.83
60/90/101	4.79	5.46
63/93	0.00	0.00
64	0.19	0.00
67	0.88	0.23
68/91	21.34	23.81
69	0.31	0.30
70	0.00	1.79
71	0.00	0.00
73	0.25	0.00
74	37.72	38.08
75	1.52	3.24
77/144	43.38	19.38
81	574.60	177.98
82/151	0.00	0.00
83/119	7.71	6.76
85/154	1007.44	1173.41
87	0.00	0.00
92	0.00	0.00
95	0.00	0.00
97	3.60	3.65
99	103.32	117.37
100	0.73	0.96
105/141	55.53	56.16
108/123	22.94	16.45
110	0.00	0.00
114	6.97	0.00
115	0.00	0.00
117	0.00	0.00
118	0.00	0.00
122/165	0.00	0.00
124	0.00	0.00
128/185	16.74	18.11
129/178	0.00	0.00
130	25.85	27.21
131	57.87	57.20
134	0.00	0.00
135	125.83	65.43
136	0.00	0.00
137	24.34	22.63
138	398.04	397.01
146	150.12	155.01
147	63.14	25.68
149	48.67	24.96
153	287.11	270.26
156	0.00	0.00
157	27.52	28.56
158	70.81	75.41
159	213.45	253.68
163	0.00	0.00
164	23.43	10.97
166	123.34	124.75
167	17.78	18.73
170	113.07	126.68

Sample ID Congener	EGG 060710	EGG 060727
172	0.00	0.00
173	12.01	9.37
174	0.00	0.00
175	23.41	23.28
176	0.00	0.00
177	30.61	32.85
179	0.00	0.00
180	460.08	467.31
183/187	183.59	169.79
189	9.13	9.89
190	75.38	77.09
191	30.91	31.37
193	0.00	0.00
194	95.13	81.54
195/207	34.67	32.71
196/203	92.43	82.80
197	10.14	9.93
199	127.98	112.68
200	0.00	0.00
202	16.63	15.25
204	0.00	0.00
205	19.48	21.43
206	70.46	53.15
208	37.77	28.95
209	12.02	8.52

Appendix 4 - Results: Statistical Analysis

Chiral Correlations

EF PCB 149 vs Fork Length: NRPK

Regression Statistics	
Multiple R	0.362516592
R Square	0.131418279
Adjusted R Square	0.064604301
Standard Error	0.052569847
Observations	15

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.00543578	0.00543578	1.96692791	0.184201225
Residual	13	0.035926654	0.002763589		
Total	14	0.041362434			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.607752653	0.116059495	5.236561249	0.000160561	0.357021359	0.858483948
X Variable 1	-0.000252609	0.000180117	-1.402472071	0.184201225	-0.000641729	0.00013651

EF PCB 95 vs Fork Length: NRPK

Regression Statistics	
Multiple R	0.202785328
R Square	0.041121889
Adjusted R Square	-0.032637965
Standard Error	0.021436601
Observations	15

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.000256192	0.000256192	0.557510443	0.468554403
Residual	13	0.005973862	0.000459528		
Total	14	0.006230054			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.459913443	0.047326011	9.717984517	2.50492E-07	0.357671812	0.562155073
X Variable 1	5.48405E-05	7.34471E-05	0.746666219	0.468554403	-0.000103832	0.000213513

EF PCB 149 vs Fork Length : NRPK Liver

Regression Statistics	
Multiple R	0.259083109
R Square	0.067124057
Adjusted R Square	-0.166094928
Standard Error	0.066794341
Observations	6

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.001284085	0.001284085	0.287815579	0.620070691
Residual	4	0.017845936	0.004461484		
Total	5	0.01913002			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.510537608	0.291154481	1.753493903	0.154384983	-0.297836827	1.318912042
X Variable 1	-0.000221898	0.000413614	-0.536484463	0.620070691	-0.001370275	0.00092648

EF PCB 95 vs Fork Length : NRPK Liver

Regression Statistics	
Multiple R	0.53829918
R Square	0.289766007
Adjusted R Square	0.112207509
Standard Error	0.027827737
Observations	6

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.001263752	0.001263752	1.631946712	0.270541632
Residual	4	0.003097532	0.000774383		
Total	5	0.004361283			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.674968498	0.121300251	5.564444347	0.00510855	0.338185009	1.011751987
X Variable 1	-0.000220134	0.000172319	-1.277476697	0.270541632	-0.000698569	0.000258301

PCB 153 Concentration vs PCB 95 EF: NRPK

Regression Statistics	
Multiple R	0.50644947
R Square	0.256491065
Adjusted R Square	0.194531987
Standard Error	0.019493781
Observations	14

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.001573111	0.001573111	4.139684996	0.064600358
Residual	12	0.00456009	0.000380007		
Total	13	0.006133201			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.483655999	0.007880827	61.37122578	2.31806E-16	0.466485153	0.500826845
X Variable 1	0.000818181	0.000402129	2.034621585	0.064600358	-5.79835E-05	0.001694345

PCB 153 Concentration vs PCB 149 EF: NRPK

Regression Statistics	
Multiple R	0.417869187
R Square	0.174614657
Adjusted R Square	0.111123477
Standard Error	0.051245973
Observations	15

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.007222487	0.007222487	2.750219115	0.121160705
Residual	13	0.034139947	0.00262615		
Total	14	0.041362434			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.471483104	0.020232633	23.30310141	5.47698E-12	0.427773157	0.51519305
X Variable 1	-0.001750015	0.001055257	-1.658378459	0.121160705	-0.004029759	0.000529729

Total PCB Concentration vs PCB 95 EF: NRPK

Regression Statistics	
Multiple R	0.024767291
R Square	0.000613419
Adjusted R Square	-0.082668796
Standard Error	0.022600588
Observations	14

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	3.76222E-06	3.76222E-06	0.007365542	0.933022665
Residual	12	0.006129439	0.000510787		
Total	13	0.006133201			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.496567612	0.011908727	41.69779273	2.34639E-14	0.470620726	0.522514498
X Variable 1	-1.13473E-06	1.32218E-05	-0.085822738	0.933022665	-2.99426E-05	2.76731E-05

Total PCB Concentration vs PCB 149 EF: NRPK

Regression Statistics	
Multiple R	0.194469148
R Square	0.03781825
Adjusted R Square	-0.042363563
Standard Error	0.05630281
Observations	14

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.001495153	0.001495153	0.471656206	0.505281547
Residual	12	0.038040078	0.003170006		
Total	13	0.039535231			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.425590501	0.029667138	14.34551924	6.46604E-09	0.36095136	0.490229642
X Variable 1	2.26211E-05	3.29383E-05	0.68677231	0.505281547	-4.91453E-05	9.43875E-05

PCB 153 Concentration vs PCB 149 EF : NRPK Liver

Regression Statistics	
Multiple R	0.591092948
R Square	0.349390873
Adjusted R Square	0.219269048
Standard Error	0.056388004
Observations	7

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.008537581	0.008537581	2.68510584	0.162216003
Residual	5	0.015898035	0.003179607		
Total	6	0.024435616			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.326416929	0.032335011	10.09484512	0.000163379	0.243297137	0.409536721
X Variable 1	0.001896081	0.001157114	1.638629256	0.162216003	-0.001078375	0.004870536

PCB 153 Concentration vs PCB 95 EF : NRPK Liver

Regression Statistics	
Multiple R	0.604255126
R Square	0.365124258
Adjusted R Square	0.206405322
Standard Error	0.026310041
Observations	6

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.00159241	0.00159241	2.300445478	0.203931412
Residual	4	0.002768873	0.000692218		
Total	5	0.004361283			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.576830772	0.038540619	14.96682673	0.000116096	0.469824858	0.683836686
X Variable 1	-0.004113872	0.002712345	-1.516721951	0.203931412	-0.011644548	0.003416803

Total PCB Concentration vs PCB 95 EF : NRPK Liver

Regression Statistics	
Multiple R	0.371016019
R Square	0.137652887
Adjusted R Square	-0.077933892
Standard Error	0.030663252
Observations	6

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.000600343	0.000600343	0.63850338	0.469011684
Residual	4	0.00376094	0.000940235		
Total	5	0.004361283			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.539213974	0.026344555	20.46775809	3.36504E-05	0.466069764	0.612358184
X Variable 1	-3.99984E-05	5.00565E-05	-0.799064065	0.469011684	-0.000178978	9.89808E-05

Total PCB Concentration vs PCB 149 EF : NRPK Liver

Regression Statistics	
Multiple R	0.59704073
R Square	0.356457634
Adjusted R Square	0.141943512
Standard Error	0.044236803
Observations	5

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.003251768	0.003251768	1.66169775	0.287775437
Residual	3	0.005870684	0.001956895		
Total	4	0.009122452			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.177267786	0.125298356	1.414765458	0.252069486	-0.221487504	0.576023077
X Variable 1	0.000450986	0.000349854	1.289068559	0.287775437	-0.000662406	0.001564377

EF PCB 149 vs Fork Length: LKWH

Regression Statistics	
Multiple R	0.717180077
R Square	0.514347263
Adjusted R Square	0.271520894
Standard Error	0.019804495
Observations	4

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.000830784	0.000830784	2.118168904	0.282819923
Residual	2	0.000784436	0.000392218		
Total	3	0.00161522			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.200436531	0.187402633	1.069550242	0.396795986	-0.605891917	1.006764979
X Variable 1	0.000603241	0.000414487	1.455393041	0.282819923	-0.001180152	0.002386635

PCB 153 Conc vs EF PCB 149: LKWH

Regression Statistics	
Multiple R	0.087365837
R Square	0.007632789
Adjusted R Square	-0.488550816
Standard Error	0.028309816
Observations	4

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1.23286E-05	1.23286E-05	0.015382994	0.912634163
Residual	2	0.001602891	0.000801446		
Total	3	0.00161522			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.478084172	0.044894467	10.64906658	0.008703187	0.284918869	0.671249474
X Variable 1	-0.001138254	0.009177378	-0.124028199	0.912634163	-0.040625322	0.038348815

Total PCB Conc vs EF PCB 149: LKWH

Regression Statistics	
Multiple R	0.411491097
R Square	0.169324923
Adjusted R Square	-0.246012616
Standard Error	0.025900994
Observations	4

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.000273497	0.000273497	0.407680277	0.588508903
Residual	2	0.001341723	0.000670861		
Total	3	0.00161522			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.497380556	0.04061734	12.24552267	0.006602788	0.322618248	0.672142865
X Variable 1	-9.94305E-05	0.000155725	-0.638498455	0.588508903	-0.000769463	0.000570602

EF PCB 95 vs Fork Length: LKWH

Regression Statistics	
Multiple R	0.6009515
R Square	0.361142705
Adjusted R Square	0.041714058
Standard Error	0.021130843
Observations	4

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.000504822	0.000504822	1.130589596	0.3990485
Residual	2	0.000893025	0.000446513		
Total	3	0.001397848			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.745936794	0.199953381	3.730553548	0.064934004	-0.114393165	1.606266753
X Variable 1	-0.000470237	0.000442246	-1.063291868	0.3990485	-0.002373067	0.001432594

Achiral Correlations

Total PCB vs $\delta^{15}N$

Regression Statistics	
Multiple R	0.674196961
R Square	0.454541543
Adjusted R Square	0.418177646
Standard Error	1041.141468
Observations	17

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	13549480.67	13549480.67	12.49980278	0.002997038
Residual	15	16259633.34	1083975.556		
Total	16	29809114.01			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-5822.973264	2022.621409	-2.878923974	0.011474536	-10134.08873	-1511.857801
X Variable 1	621.1981403	175.7027531	3.535506014	0.002997038	246.6965888	995.6996918

PCB 153 vs $\delta^{15}N$

Regression Statistics	
Multiple R	0.581634373
R Square	0.338298544
Adjusted R Square	0.294185114
Standard Error	86.39916872
Observations	17

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	57246.43223	57246.43223	7.668833297	0.014319988
Residual	15	111972.2453	7464.816356		
Total	16	169218.6776			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-398.6144494	167.8473231	-2.374863311	0.031324773	-756.3725483	-40.85635056
X Variable 1	40.37783553	14.58070039	2.769265841	0.014319988	9.29980845	71.45586261

Total PCB vs δ^{15}N : LLB Fish

Regression Statistics	
Multiple R	0.806691184
R Square	0.650750666
Adjusted R Square	0.615825732
Standard Error	164.4036492
Observations	12

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	503618.8076	503618.8076	18.63283912	0.001521275
Residual	10	270285.5987	27028.55987		
Total	11	773904.4064			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-1130.515382	376.1794181	-3.005255809	0.013224362	-1968.695355	-292.3354083
X Variable 1	147.9119813	34.26603369	4.316577245	0.001521275	71.56250068	224.261462

PCB 153 vs δ^{15}N : LLB Fish

Regression Statistics	
Multiple R	0.861196723
R Square	0.741659795
Adjusted R Square	0.715825775
Standard Error	3.984878665
Observations	12

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	455.8720242	455.8720242	28.70864779	0.000319919
Residual	10	158.7925797	15.87925797		
Total	11	614.6646039			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-40.10036342	9.117980924	-4.397943333	0.001339358	-60.41649088	-19.78423596
X Variable 1	4.450141856	0.830553259	5.358045146	0.000319919	2.599553879	6.300729832

Total PCB Concentration vs PCB 153 Concentration : DCCO Chick

Regression Statistics	
Multiple R	0.158920734
R Square	0.0252558
Adjusted R Square	-0.949488401
Standard Error	339.0553338
Observations	3

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	2978.59615	2978.59615	0.025910182	0.898397141
Residual	1	114958.5194	114958.5194		
Total	2	117937.1155			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	1767.227573	4206.142593	0.420153985	0.746778833	-51676.88136	55211.33651
X Variable 1	7.522766466	46.73501095	0.1609664	0.898397141	-586.3018509	601.3473839